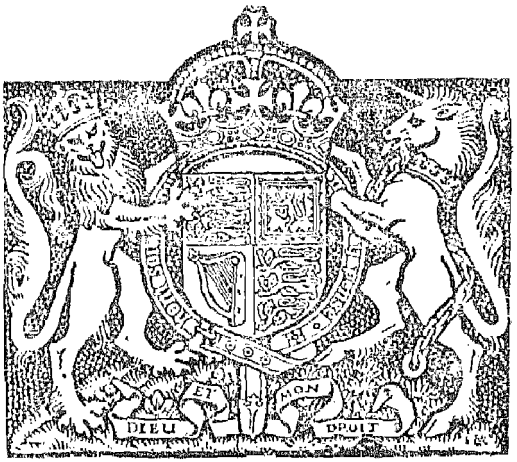

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VARNISH CONSTITUENTS

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BY

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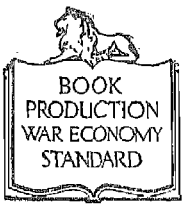

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FOREWORD

THE view has often been expressed that the Symposium on Varnish Making, held by the Oil and Colour Chemists' Association at Harrogate in 1939, marked a milestone on the road to a better knowledge of the manufacture of varnishes and varnish media. It is well, therefore, that some consideration should be given to lessons learned at that Conference. Outstanding amongst these, perhaps, was that apparent gap in our knowledge of the manner in which the chemical and physical aspects of the subject could be more strictly and more accurately correlated. What was evident was that such correlation must be based in the first instance upon a sound knowledge of both the chemical and physical properties of the constituent materials.

Thus we see how necessary it is that we should acquire as complete a knowledge as possible of the raw materials with which we have to deal. It is only by doing so and by learning the correct methods to adopt in their employment that such materials can be utilised to their greatest advantage.

The advance in our knowledge of the fundamental nature of polymerisation and resinification and the growth of the chemical industry, whereby new chemicals have become commercially available, have contributed not only to an increase in the production of new materials in recent years but to a marked improvement in those now long established.

For some years now the trend has been such that the manufacture of the raw materials for varnish making has become more and more specialised, and there has been a resultant tendency towards that divergence in knowledge which specialisation is liable to promote. True progress, however, can only be achieved if the technical skill of the varnish maker is closely associated with the researches and developments of the raw material manufacturers. For this reason it is indeed necessary that the technologists working in the different fields should co-ordinate their efforts towards the common end.

To do this it follows that those engaged in the manufacture and development of raw materials should themselves know something of the purpose for which they are intended. But it means more than that because, as a natural consequence of specialisation, it is evident that what the varnish chemist or technologist has been pleased to regard as his raw material is to-day a finished product of manufacture in which both skill and knowledge have already been applied.

This is something we should do well to appreciate. We should also recognise its implications for, in so far as the chemical and physical characteristics of a given varnish are predetermined in a large measure by the chemical and physical properties of the basic constituent materials, it is evident that the manufacture of these raw materials is itself playing

an ever more important part in the progressive development of the varnish and paint industry and its allied trades. In other words, in reality varnish making to-day commences at a still earlier stage, and a detailed study of the basic constituent materials becomes a definite pre-requisite of successful achievement.

This review by Dr. Chatfield of the present position in regard to the various raw materials used for varnish making and surface coatings will therefore earn him the gratitude of many technologists in the industry. In its compilation the author has made a valuable and exhaustive digest of the more important published information, and has welded it into a form which presents a clear picture of the developments which have been taking place throughout the whole field. To achieve this within the confines of a single volume can have been no easy task, and certain shortcomings would seem to have been inevitable. To meet this difficulty, however, the author has given numerous references and any such omissions as may exist cannot detract from its main value.

This is at once a book for the student seeking knowledge of the subject, for the practical man requiring technical information which is not too fundamental in character, and for the more advanced technologist or chemist who by means of the ample references given has at his disposal a great deal of detailed information against the necessary fundamental background. Dr. Chatfield is to be congratulated upon the results of a very painstaking work.

W. ESMOND WORNUM.

TETTENHALL,
STAFFS.

PREFACE TO THE SECOND EDITION

A SECOND edition has enabled me to add technical information on a number of new subjects, and to elaborate, correct, and adjust some of the existing ones.

It would have been easier to reprint a corrected first edition, but the response and kindness with which my modest volume was received, encouraged me to expand it very early in its life. I hope thereby to increase its utility.

Development to-day is moving at such a rapid pace, that with the printing and binding trades hopelessly overburdened with work, a volume on a technical subject is, unfortunately, a little out of date on publication. In this unavoidable deficiency I beg for an allowance to be made by my readers. Nevertheless definite trends in the industry can now be detected, which previously were partly eclipsed by essential war influences.

The chapter on "Varnish Oils" has been considerably enlarged, and this is chiefly because of the inclusion of information on the new Processed and Synthetic Drying Oils, some of which, by reason of obvious merit, have apparently come to stay. The search for substitutes for the old and well-tried drying oils has also brought to light many new, useful natural oils, some possessing very interesting properties. Vegetable oils like grapeseed oil, hardly of recognised value before 1939, have been used successfully for the past few years in Continental varnishes. Tall oil has also received considerable attention in America, Germany, and elsewhere, in an effort to eke out low stocks of bonafide vegetable oils.

The sections on rosin, turpentine, and shellac have been revised, and in this revision the assistance of W. Garvie, Esq., is gratefully acknowledged.

Hydrogenated and polymerised rosins are increasing in favour, and more information is now available. De-hydrogenated rosin is another new-comer to the field. Recently developed products which promise to become valuable alternatives to the well-established rosin esters, are those derived from polymerised rosin with glycerol, pentaerythritol, and other polyalcohols.

Zein, an alcohol-soluble protein, has found for itself a permanent place among the relatively few spirit varnish resin constituents of natural origin. Substantial quantities are already being used in lacquers in the Western hemisphere.

Among the newer synthetic resins, those based on cashew nutshell liquid have firmly established themselves on both sides of the Atlantic and information on them is now included. Other synthetic resins which are attracting interest are the polyamides, and those containing silicon.

Varnish Constituents

The tables of constants of proprietary brands of synthetic resins have been enlarged very considerably, and include most British and many American products.

Among the solvents rationalisation of the many petroleum fractions has occurred, and full information has been published on a very useful range of special boiling-point spirits (S.B.P.S.). The nitroparaffins now available commercially are interesting by reason of their exceptional solvent power for certain types of synthetic resins.

Chlorinated paraffin waxes have joined the chlorinated naphthalenes as varnish constituents with special applications.

H. W. CHATFIELD.

CROYDON, *October*, 1946.

AUTHOR'S PREFACE

DURING the past twenty years, varnish making has developed in an astounding manner. Considerable research has been undertaken by raw material suppliers and others, and the varnish maker has been presented with an extensive array of valuable raw materials, which have not, as yet, been developed to full advantage.

It is a formidable task to keep abreast of all published information, but the temporary reduction of progressive research work, consequent upon war conditions, affords an opportune time at which to take stock.

This volume is a modest attempt to review the more important developments of recent years, and to blend these into a composite whole with all that is of value from the remoter past.

I have long felt the need, personally, for collected information. Varnish making is of such importance to-day, that it merits, unquestionably, special consideration. The wide expansion in scope, of varnishes, with the raw materials involved, has caused the consumer to consult many different sources for information. I have endeavoured to provide this information as concisely as possible in one volume.

Generally, theories and hypotheses have been excluded. Aspects of the subject which are primarily academic, such as the mechanism of the drying process, the precise mechanism of resin formation, or evidence providing information on chemical constitution have not been expounded in detail. For those who wish to pursue these subjects further, the foundations of study are available in the references given.

It is my firm conviction that the more knowledge a varnish technologist accumulates about the manufacturing details and properties of the available raw materials, the easier the elucidation of a particular formulation problem, and the greater the chances of the correct prediction of the cause of a defect.

The subject-matter has been designed to be of use to a wide circle of people in the Varnish Making and Allied Trades. In addition to the technologist, it is my profound hope that both student and manager will discover much of value also.

I have presumed to dogmatise and criticise as little as possible, but rather to present the intelligent reader with most of the evidence, from which his own conclusions may be drawn.

In the compilation of this work I have received encouragement and assistance from many friends in the industry. It is, therefore, my bounden duty to place on record my deep appreciation and thanks for generous assistance so readily given.

In this connection, I should like to express my thanks to Esmond Wornum, Esq., M.C., B.Sc., A.R.C.S., F.I.C., for doing me the honour of

writing a Foreword, and to the following gentlemen for their criticism and advice :—

C. W. A. Mundy, Esq., A.I.C., of Younghusband, Barnes & Co. Ltd., on " Varnish Oils," " Monoglycerides " and " Antioxidants."

J. D. Morgan, Esq., B.Sc., of British Resin Products Ltd., on " Phenol Formaldehyde, Urea Formaldehyde, Polystyrene and Coumarone Resins."

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And to :—

C. H. Birkitt, Esq., B.Sc., A.I.C., F.I.R.I., of Rubber Control, Ministry of Supply, and R. C. Moakes, Esq., B.Sc., of the Research Association of British Rubber Manufacturers, on " Rubber."

My thanks are also due to L. A. Hughes, Esq., Ph.D., A.R.C.S., and H. F. Day, Esq., A.R.C.S., B.Sc., of Jenson & Nicholson Ltd., for checking tables and reading proofs, respectively, and to the British Standards Institution for permission to include extracts from specifications.

I also appreciate greatly the assistance afforded me by Raw Material and Plant Suppliers in providing photographs and diagrams, and British Resin Products Ltd., Kestner Evaporator & Engineering Co. Ltd., W. J. Fraser & Co. Ltd., Shell Mex & B.P. Ltd., Watts Ltd., and Aluminium Plant & Vessel Co. have kindly co-operated in this way.

Finally, I am indebted to Miss C. Warren who undertook the task of preparing the typescript from a difficult manuscript, and for her assistance in the compilation of the indices.

H. W. CHATFIELD.

WADDON,
SURREY, May 1943.

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CHAPTER 1

VARNISH OILS

SCARCITY of tung oil has proved a great incentive to the investigation for substitutes, and while only one complete substitute has been discovered, oils new to the trade, with valuable properties, have been unearthed. It should be recorded, however, that Trienol, the substitute in question, has never been available in commercial quantities. Irregularity of supplies of tung oil even in peace-time, lately aggravated by the Chinese "incident" and the World War, and its high price, have done much to precipitate periodic scrambles for substitutes. In Germany the scarcity of vegetable oils generally, has stimulated efforts to reformulate protective coatings with a minimum content of vegetable oil or with synthetic substitutes.

China, at times practically isolated during the upheavals of war, has been forced to consume a substantial part of her tung oil crop for her own vital needs. It is reported that at least half of her tung oil is cracked to yield motor spirit, diesel oil and lubricants, and that projects are afoot to use it as a basis for the production of synthetic rubber.[147] It will be interesting to see whether these war-time expedients are considered economic propositions in peace. If so, then some of the changes in products which have been forced on the varnish trade of the world in the past few years may become permanent, and the trend of varnish formulation may swerve violently in directions other than along the course into which tung oil has influenced it in the past. It is heart-breaking for technologists to watch tung oil, valued at several hundred pounds per ton, cracked for fuel!

In spite of disturbing influences, linseed oil, by reason of its abundance, and the careful organisation of its distribution, remains the most popular varnish oil. Moreover, it is difficult to visualise any great diminution of its importance in the immediate future, for even assuming a markedly increased interest in alkyd varnishes to the detriment of the natural gum products, it is logical to anticipate that linseed oil, directly, or indirectly through its derivatives, the fatty acids or monoglycerides, or as the basis of new synthetic oils, will still maintain the pride of place which it has held for centuries.

LINSEED OIL

Source.—Linseed oil is derived from the flax plant, *Linum usitatissimum*, which is grown in the Argentine, the United States of America, Russia, India, Canada, Belgium and Germany. It has been grown also in New Zealand, China, Irak, Yugoslavia, around the Danube, and in

Special Note.—The physical constants of the oils are included in the table at the end of this chapter.

Kenya. The most important sources of supply are the first four named. It is interesting to note also that the production of flax is increasing in the United Kingdom. The yield of oil is sub-normal because the seed is harvested green, but it has been predicted that the production may become important.[232]

Composition.—The approximate percentage composition of its fatty acids is :

	Per cent.[1]
Saturated acids	8·7–11·3
Oleic acid	4·8–18·8
Linoleic acid	23·2–62·3
Linolenic acid	24·2–50·2

The oil is obtained from the seed chiefly by pressing, but sometimes by solvent extraction.

Raw Linseed Oil

Raw linseed oil is not used to any appreciable extent in the manufacture of varnishes. It is the crude product expressed from the seed and usually without much subsequent treatment. It is used only in processes where the presence of traces of water or mucilaginous matter are unimportant, e.g. in the preparation of paints, putty, and metallic soaps by hydrolysis and precipitation. When the mucilaginous matter, "spawn," "break," or "foots," which is believed to consist of carbohydrates, albuminous material, and phosphatides, is removed, the resultant oil is the refined oil of the varnish trade.

The colour of the expressed or extracted oil increases in intensity with the temperature of these operations.

Refined Linseed Oil

Raw oil is refined either by tanking for long periods, or by acid or alkali treatment. Raw oil "breaks" on heating to 260° C. or higher, a process which may be facilitated by the presence of traces of water or glycerol. Some varnish makers buy a good grade of raw oil, subject it to this heat treatment, filter off the precipitated "break" and use the refined oil for the production of varnishes or stand oil.

The separation of "break" during subsequent treatment of linseed oil can be prevented [2] if the raw oil is heated with about 20 per cent. of polymerised oil at 80°–120° C. for sixty to ninety minutes. The polymerised oil may be heated castor oil, linseed stand oil, soya bean stand oil or tung oil stand oil. Alternatively, the same object may be achieved, according to Mundy, by increasing the acidity of the raw oil. The amount of "break" obtained from raw oil varies from 0·17 to 0·23 per cent.[3]

The colour of the natural oil can be improved by heating or mixing with decolorising earths like fuller's earth (up to 1 per cent.), or heating with anhydrous absorbent magnesium silicate.[217] Oils can, of course, be bleached by exposure to sunlight, but in these days of increasing bustle, this method is hardly a commercial proposition.

Oils containing carotenoid pigments can be bleached by hypophosphorous acid (0·02–0·10 per cent.), or its monobasic salts. A temperature of 220°–255° C. is used and the operation is preferably conducted under vacuum.[231] Treatment of vegetable and animal oils with an alkylolamine, followed by removal of the compound formed by washing with alkali, and then with water, provides oils which are freed simultaneously, from both colouring matter and free fatty acids. Other bleaching agents include hydrogen peroxide (0·3–1·5 per cent.), and sodium nitrite (0·4–2·0 per cent.).[235] Treatment with alcoholic alkali has been suggested as means of reducing acidity but the effect on colour of this treatment is not recorded.[238]

Sometimes, in filtering oils with the use of filter aids of diatomaceous silica types, darkening is caused by contact with the filter aid. This darkening, according to a recent patent, is prevented if a trace of citric acid is added during filtration.

Long storage trials, lasting up to one year, conducted in India, on various vegetable oils in different containers, indicated that deterioration occurred most in metal containers (tinned and ordinary steel), and least in glass. There was a most noticeable increase in viscosity of the oils in the steel containers, and this varied according to the tendency of the oil under test, to oxidise. Peroxide values were also determined, and these increased during the early months of storage and then decreased. The oils examined were linseed, ground nut, and cottonseed, and it is reasonable to assume that the extent of the deterioration under the hot Indian conditions would be reduced in more temperate climes.[233]

Boiled Linseed Oils

These are made by blowing the oil at 90°–150° C. in the presence of soluble lead and manganese salts. Some types such as pale boiled oils are blown in the absence of driers. Boiled oils vary in gravity (0·940–0·950), depending upon the extent to which they have been treated. They are rarely used in varnish manufacture. Their chief uses are in the manufacture of asphaltum finishes, in paints, and in special finishes for cotton fabric and silk.

Stand Oils

Preparation.—Stand oil is a heat polymerised linseed oil where little or no simultaneous oxidation has been allowed to occur. Refined oils only are used for such treatment, since upon heating raw oil, deposition of " break " takes place. This may decompose or char at the bottom of the boiling vessel, causing discoloration and a risk of fire. A satisfactory refined oil suitable for stand oil production should show no signs of " break " on heating to 300° C., and should bleach quite appreciably in the process.

Stand oils may be made at any temperature between 250° and 310° C. Below 250° C. the rate of polymerisation is slow and the procedure is uneconomical, and above 310° C., unless the duration of heating

at this temperature is reduced considerably, destructive decomposition becomes apparent. The rate of polymerisation over the range 250°–310° C. is such that strict laboratory control is possible. With a care-

TEMPERATURE OF POLYMERISATION, 250° C.[1]

Time of Heating (Hours).	Acid Value.	R.I. at 68° F.	Sp. Gr. 20° C./15.	Viscosity at 20° C.	Thinner Reduction Figures (20° C.).
0	1·01	—	0·9290	<1·0	—
22	2·10	—	—	2·0	—
43	2·61	—	—	15·6	12
50	2·80	—	0·9626	26·9	17
64	3·00	—	0·9696	118·5	31
70·5	3·30	—	0·9711	370·0	41
*73	3·48	—	—	—	64
TEMPERATURE OF POLYMERISATION, 290° C.					
1	1·94	1·4820	—	1·15	—
2	2·07	1·4832	0·9363	1·55	—
4	2·47	1·4853	0·9446	3·3	0·5
6	2·98	1·4871	0·9524	9·0	7·0
8	3·43	1·4898	0·9600	23·0	14·5
9	3·59	1·4902	—	44·0	18·0
10	3·84	1·4912	0·9660	82·0	22·5
11	4·39	1·4921	—	153·0	28·5
11·5	4·75	1·4923	0·9696	196·0	31·5
TEMPERATURE OF POLYMERISATION, 300° C.					
1	2·78	1·4825	—	1·45	—
2	3·08	1·4846	0·9413	2·25	—
4	3·58	1·4872	0·9525	8·5	7·5
5	4·09	1·4889	—	20·0	12·0
5·75	4·75	1·4899	0·9607	32·0	15·5
6·75	5·56	1·4916	—	80·5	22·5
7·75	6·41	1·4926	0·9682	180·0	28·5
8·10	6·82	1·4928	0·9702	262·5	31·5
TEMPERATURE OF POLYMERISATION, 310° C.					
1	2·63	1·4834	0·9396	1·9	—
2	3·43	1·4871	0·9497	6·7	4·7
3	3·94	1·4885	0·9569	17·0	11·0
4	4·54	1·4901	0·9625	43·5	18·0
5	5·56	1·4915	0·9675	128·5	25·5
5·25	6·11	1·4923	—	164·5	27·5

Viscosity figures represent poises very approximately. Thinner reduction figures represent the c.c. of white spirit required to reduce 50 c.c. of the stand oil to a viscosity of 3·0 at 20° C.

fully tested refined oil, a good standard plant, e.g. a Sommer plant, and accurate temperature control, consistent batches of stand oil can be produced at 300° C. approximately, with but little intermediate testing.

* At this point the oil was stringing rapidly and was almost completely gelled on cooling.

The preceding figures [4] show the physical changes which take place during the heat polymerisation of linseed oil. The oil was bodied in an aluminium pot, stirred continuously to avoid local overheating, and connected to a fairly strong exhausting draught so that the oil was in permanent contact with air at its surface. The pot was gas-heated. The progress of polymerisation was followed by the determination of physical constants.

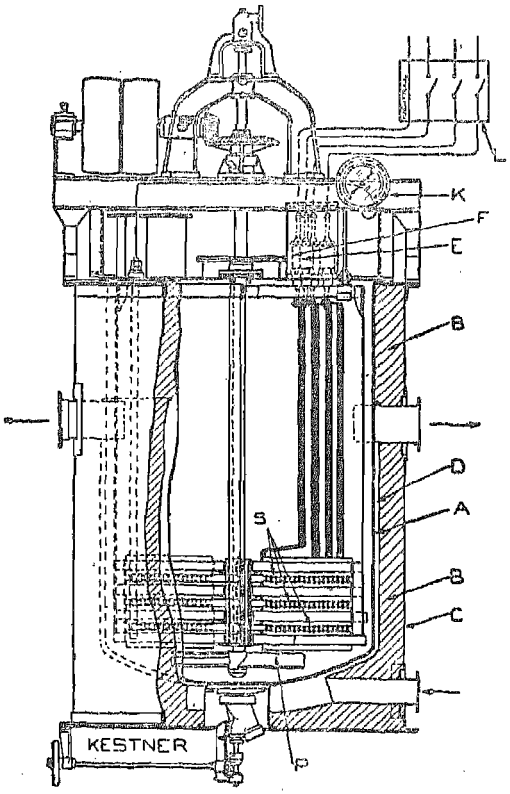
It can be deduced, therefore, that the process of polymerisation takes place simultaneously with increases in acid value, specific gravity and refractive index. For all temperatures there is a period of induction in which no appreciable increase in viscosity is observed, and its duration varies inversely as the temperature of polymerisation. The induction period may be caused by one of two influences, or possibly both. During the period of apparent inhibition of the polymerisation process, natural polymerisation inhibitors may be decomposed by the high temperatures involved, and/or the isolated double bonds may be converted into conjugated bonds. In other words, the now popular mechanism of isomerisation occurs. Oils containing conjugated double bonds polymerise more rapidly than those with isolated ones. The more elevated the temperature the greater the speed of polymerisation, e.g. for an oil of approximately 118 poises at 20° C., sixty-four hours are necessary at 250° C.; between ten and eleven hours at 290° C.; between 6¾ and 7¾ hours at 300° C.; and about five hours at 310° C. For the rapid production of a good quality stand oil 310° C. is a very convenient temperature. The views of Bradley upon polymerisation are generally accepted.

Uniformity.—Uniformity in the polymerised oil is controlled largely by the conditions of polymerisation. Fierce direct heating should be avoided and the oil should be stirred continually. Failure to note these precautions will result in stand oils which are mere dispersions of highly polymerised molecules in slightly polymerised molecules.[5]

Type of Pot. Method of Heating.—Much "open pot" stand oil is made by heating the oil at approximately 300° C. in mild steel, stainless steel, aluminium or copper pots. Copper bottoms are frequently fitted to mild steel pots. The method of heating may be by means of coke, coal, gas or oil. Klatte [6] favours the use of gas in place of solid fuels which he claims are difficult to control. In general, this is true, but heating by solid fuel such as coke is controllable if the pot can be raised by adjustable trolleys in the hands of experienced workmen.

Colour.—The colour of stand oil is a controllable property. Metals which tend to be attacked by fatty acids at high temperatures to form coloured compounds should be avoided, if freedom from discoloration is desired. Oxidation products of oils are known to be highly coloured, and these can be prevented by conducting the polymerisation in an atmosphere of carbon dioxide. Considerable investigation in recent years has shown that, in the presence of catalysts, normally stable bodies are

oxidised to yield, among other products, fatty acids. The most efficient catalysts are compounds of the so-called "drying metals," lead, cobalt and manganese. It is known also that iron acts as an oxidation catalyst at elevated temperatures, and hence it is reasonable to assume that the formation of compounds of iron during stand oil production will assist in oxidation and promote fatty acid formation. As the concentration of fatty acid increases, the more prolific will be the formation of iron salts. Copper pots may also cause discoloration. Thus stainless steel or aluminium pots should be used, and from the foregoing it is apparent that if the pots have been used in other varnish-making processes, they should be cleaned scrupulously free of undissolved compounds of the drying metals. For ease of cleaning, stainless steel is much superior to aluminium since it can be boiled with caustic soda. In choosing aluminium or stainless steel for the pots, the pot covers, thermometer cases and stirrers should be of the same metal. Oils which have been contaminated with metallic impurities such as compounds of iron and nickel, can be refined and their colour improved by warming with solutions of certain organic acids, and blowing with air. Suitable acids are lactic, citric or tartaric. The impurities can be filtered off as complex metallic precipitates.[234]



KESTNER "ISOLECTRIC" PATENT HEATING PLANT.

A—Vessel. B—Lagging. C—Outer casing. D—Outer jacket. E—Terminal. F—Neutral terminal. P—Paddles. S—Heating elements.

Fierce direct heating causes local overheating at the bottom of the pots with consequent destructive decomposition and darkening. Its effect may be minimised by vigorous agitation. Lagging of the radiating surface of the pot will reduce the heat necessary to raise the oil to the required temperature.

Refined linseed oil usually bleaches on heating to 300° C., but maintenance at this temperature causes gradual discoloration.

Special Stand Oil Plants.—Special plants have now been constructed to produce pale uniform stand oils. A popular one is the Sommer-Schmidding. It consists essentially of an enclosed system where the space unoccupied by oil is filled with an inert gas such as carbon dioxide or nitrogen. The bodying vessel is filled nearly completely, and provision is made for overflow due to expansion, by attaching a smaller collecting vessel. The oil is kept agitated by means of the stream of inert gas. This system produces very pale unoxidised oils.

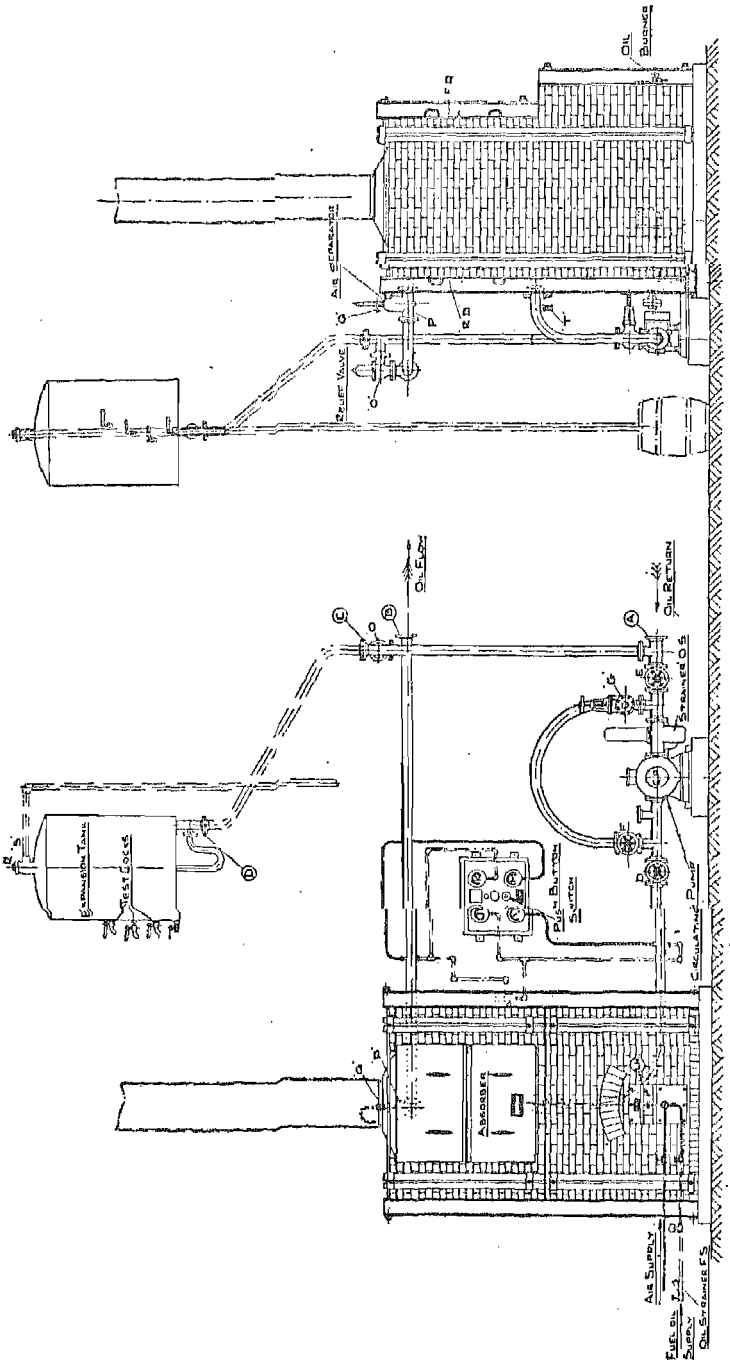
The Kestner "Isolectric" Patent Heating Plant shows another important advance in stand oil technique. The oil is heated electrically by immersion heaters, and where electricity rates are low the plant is a valuable acquisition. The heating elements are arranged so that the conducting surface is very much larger than that of a direct fired pot, which means that the source of heat operates at a much lower maximum temperature. Local overheating and destructive decomposition are thus reduced to a minimum. The shape of the elements allows free thermal movement of the oil. Waste of heat is prevented by efficient lagging to prevent radiation losses, and it is claimed that by the system of heating employed, the heating efficiency is almost 100 per cent. The stand oils produced are of excellent uniformity and colour. Both with the "Isolectric" and the Sommer-Schmidding plants, fire risks during manufacture are reduced to a minimum. The Isolectric system of heating has been applied to Sommer plants with good results.

Other patented methods of heating which avoid local overheating are those based on the familiar steam circulating system, except that liquids other than water are used. Therefore, higher working temperatures are possible. The liquid is vapourised in a generator, circulated around the vessel to be heated and is subsequently returned to the generator. The Kestner Evaporator and Engineering Co. Ltd. employ a liquid described as "Perolene," the vapour of which can be generated over the range 260°–415° C.

	Temp.	Press (lb. per sq. in.)
Perolene . . .	315° C.	40
	415° C.	200
Steam	315° C.	1530
	415° C.	>200 atmospheres

Another installation working on a similar principle is known as the Dowtherm Heating System. The heating medium in this case consists of diphenyl, diphenyl oxide, or the eutectic mixture. This system is explained in greater detail in Chapter 7 (Alkyd Resins).

Where lower temperatures are required the Merilene system of fluid heat transmission may be used. It consists essentially of transferring heat to an oil which is circulated around the vessels to be heated. The attainment of temperatures up to 315° C. is claimed.



Merilene Patent Heating Unit.

A—Return main. B—Supply main. CP—Positive rotary pump. OS—Strainer. F—Valve. H—By-pass. P—Air separator.

A method has been patented for the production of stand oils from linseed, soya and similar oils, which, according to the claims, enables unrefined oils to be used without risk of break formation. The oil is continually fed and thoroughly mixed into a volume of oil which is maintained at the bodying temperature. Carbon dioxide is bubbled through simultaneously to effect removal of acidic decomposition products, and the bodied oil is withdrawn at the same rate as the raw oil is admitted.[250]

Acidity of Stand Oils.—The chemical changes occurring during polymerisation are very complex. Many postulations have been advanced but, as yet, no unanimity of opinion exists. There is no doubt that some decomposition of the triglycerides takes place to provide free fatty acid. In open pot stand oils atmospheric oxidation may be a contributory cause of generation of fatty acids, catalysed by the presence of traces of metallic compounds which, as indicated already, may be present if the heating is conducted in mild steel pots. It is obvious, however, that oxidation is not the main cause of fatty acid formation since fatty acids are formed during polymerisation in inert atmospheres, as the result of a complex disruption of the triglycerides.

With open pot oils if a good draught is used, the acid value of the final stout stand oil will be of the order 6–8. Some fatty acid distills off and may be detected in the fume extraction system. With oils produced in the Sommer-Schmidding plant the acidity is determined largely by the rate at which the inert gas is passed.

Turbidity.—Steger and Van Loon [7] have studied the turbidity of stand oils and believe it to be due to the presence of saturated fatty acids or to the rather more highly saturated triglycerides. The amount of the acidity of the stand oil controls the degree of turbidity. The saturated free fatty acids which may be liberated during the polymerisation are not completely soluble in stand oil at normal temperatures. Similarly, the more highly saturated triglycerides, whilst being soluble in the unpolymerised oil, are less soluble in stand oil and demonstrate their presence by partial precipitation. The saturated fatty acid content of the untreated oil determines the ultimate degree of turbidity. During the polymerisation process, whilst still warm, and often for days afterwards, stand oils of normal acidity remain clear. The development of turbidity is usually very slow.

Ulrich [8] agrees generally with the above findings. He believes that turbidity is due to the rearrangement of the naturally occurring mixed triglycerides to more saturated types, or to the elimination of saturated fatty acids. Since both saturated triglycerides and acids have higher melting-points than similar unsaturated compounds, their tendency to precipitation is greater. Ulrich disagrees, however, that turbidity is controlled by acidity.

The turbidity of stand oils is not usually regarded as a serious defect.

Their incorporation into varnishes with resins and thinners considerably minimises the tendency to turbidity, and a short ageing of the varnishes obtained, followed by filtration through a press, removes the defect completely.

Control of Degree of Polymerisation.—The degree of polymerisation of linseed oil is an easily controllable property. In practice, most manufacturers are content to use viscosity as the most suitable guide to the extent of polymerisation. For speed and reliability the Gardner-Holdt tube method for viscosity determination is probably the most satisfactory. It consists, essentially, in filling to a given mark a standard tube with the oil to be tested, and cooling it with a similar tube containing a liquid of known viscosity, for approximately ten minutes at a specified temperature. The two tubes are inverted and the speeds of travel of the air bubbles through the liquids compared.

Accelerated Polymerisation.—Much work has been done on catalytic and accelerated polymerisation of linseed oil. It is said that neutral oils are not suitable for stand oil formation and that the most convenient oils have an acid value of 0·5–2·0. The presence of acid is said to accelerate the speed of polymerisation. Other workers, however, believe that the presence of acid has a retarding and peptising effect upon polymerisation. With fish oil it has been found that the rate of polymerisation varies inversely as the concentration of stearic acid.[9] The discrepancy of opinion is probably explained by the difference in amounts of acid present.

Oil is passed over catalysts at the temperature of polymerisation, and the catalysts, which may be in aggregated form, include nickel, platinum, palladium, cobalt, iron, copper, aluminium trichloride, stannic chloride, and antimony trichloride.

Temperatures of 260°–320° C. are used for the catalytic polymerisation of drying oils using active nickel. Similarly, a temperature range of 200°–320° C. is suggested for use with nickel formate or platinised asbestos.[10] Catalysts in active form are also produced by dispersing metals in a suitable liquid (butyl alcohol, propyl alcohol or turpentine), by means of an oscillating discharge. The metals used may be cobalt, iron, manganese, lead, nickel, tungsten, chromium and molybdenum. For cobalt dispersions, an addition of 0·01 per cent of metal may be used and the polymerisation carried out in an atmosphere of carbon dioxide at a temperature of 280° C. for eight hours.[11] Other protected catalysts are mercapto-benzthiazol (0·2–1·0 per cent), diphenylguanidine (0·1–0·5 per cent), amines, organic disulphides, maleic anhydride, boron trifluoride, anthraquinone and aluminium naphthenate.[12] The effectiveness of anthraquinone as a polymerisation catalyst is illustrated by the experimental results of Hewitt and Cottrell.

They heated alkali refined linseed oil (vis. 0·5 ; poises at 25° C. ; A.V. 0·44 ; I.V. 181·3) in an open glass flask at 307° C. with 0·1 per cent of anthraquinone. The results are given in the facing page.[252]

The same workers reported that calcium linoleate (0·3 per cent) was about as effective as anthraquinone, but it had the disadvantage of causing darkening.

Wilborn has reported that a whole series of metallic resinates have a beneficial catalytic effect on the polymerisation rate of linseed oil during stand oil manufacture. The following is a complete list of the resinates arranged in order of effectiveness, the most effective being placed first: thorium, lead, nickel, cobalt, iron, calcium, manganese, chromium and uranium.[211] If claims are true, sodium oxalate (5 per cent) heated with oil at 300°–350° C., actually yields a solid product.[210]

Hydrochloric acid and sulphur dioxide have been used satisfactorily, but sulphur dioxide is preferable since hydrochloric acid promotes hydrolysis, and produces oils of high acidity containing chlorine which are dark in colour. Sulphur dioxide gives oils of low acidity and pale colour, with a sulphur content of less than 0·1 per cent. Sulphur dioxide has other advantages in that it is cheap, easily recovered, and cannot be poisoned. At 290° C. in the presence of sulphur dioxide the rate of

Hours at 307° C.	Viscosity (poises at 25° C.).		Acid Value.		Iodine Value.	
	Catalyst	No catalyst	Catalyst	No catalyst	Catalyst	No catalyst
2½	1·65	1·4	2·58	1·77	159·0	159·5
4½	8·5	6·3	2·79	2·00	140·7	143·0
6½	36 approx.	25 approx.	3·61	2·32	—	—
7½	63 approx.	40 approx.	4·26	2·76	108·0	115·5

increase in viscosity is doubled. The induction period of pilchard oil is removed if the oil is treated with dry sulphur dioxide.[13] At 290° C. both sulphur and selenium (0·3 per cent) have been found to act catalytically on the speed of polymerisation of linseed oil.[14] Sodium bisulphate (0·4–0·5 per cent) has been found advantageous in the production of fish oil stand oils at 275° C.[15] Oxygen is a polymerisation catalyst and is considered one of the most effective.

Oils containing polymerisation catalysts, are marketed under the name "Catalysed oils."

Retardants.—Some substances hinder polymerisation and these include the resinates and linoleates of mercury, barium, strontium and copper. When polymerisation is accompanied by oxidation as in blowing, the presence of cobalt linoleate (0·1 per cent cobalt), anthranilic acid (1·0 per cent), quinol (0·25 per cent), or phenylhydrazine (0·1 per cent) retards polymerisation.[16]

Effect of High Temperatures.—Accelerated polymerisation has been attempted also by subjecting the oils to temperatures in excess of 300° C. One method is to heat rapidly flowing oil to a high temperature, to

maintain the temperature and to cool quickly.[17] The process can be made continuous, as with the Kestner Continuous Oil Polymerisation Plant. For polymerisation of linseed oil temperatures of 375°–385° C. are used, and the duration of treatment is approximately thirty minutes, for the production of a stand oil requiring from eight to ten hours under normal conditions. Temperatures up to 450° C. for four to ten minutes have been suggested also.[18]

Effect of Pressure.—Increased decomposition consequent upon elevation of temperature has been prevented by simultaneous increase of pressure. Pressures of 3,000 atmospheres, and 500 to 1,200 atmospheres [19] have been included in protected processes.

It is claimed, in addition, that polymerisation is accelerated if subnormal pressures and normal temperatures are used, and that danger of spontaneous ignition is eradicated. At 300° C. and 10 mm. acidic decomposition products and some unpolymerised or partly polymerised substances are removed. Another protected process uses a temperature of 290°–300° C. and a pressure of 2–5 mm.[20] Polymerisation under light vacuum (740 mm.) also results in acceleration of the process and yields stand oils of low acid value.[21]

Effect of High Frequency Current.—Subjection of thin films of oil to a high frequency alternating current has been suggested as a means of promoting polymerisation.[22]

Improved Stand Oils

Modifications in method have produced improvements in the quality of stand oils. Ordinary unprocessed stand oil as generally available is, in reality, a heterogeneous mixture of free fatty acid, and glyceride agglomerates of varying degree of association.

Solvent Extraction.—Solvent extraction has been used to improve the homogeneity. The unpolymerised phase of stand oil, the saturated portion, and the free fatty acids, are soluble in acetone, ethyl, butyl and amyl alcohols, and diethyl malonic ester.[23] The more highly polymerised and unsaturated residue is claimed to have better drying properties and to be more water resistant than the unextracted oil. Extracted oils have been marketed under the name "Tekaol." Work by Eibner has illustrated the instability of these oils but they now seem to be enjoying some popularity. Further information on solvent extracted oils is given on page 34.

Distillation.—It is claimed that the free fatty acids generated during stand oil formation can be removed by steam distillation.[24] The most promising results of stand oil improvement have been made by subjecting the stand oil to a high vacuum distillation,[25] and this aspect of the subject is also elaborated later, in the section devoted to Processed and Synthetic Oils. One method effects the removal of free fatty acids by spraying the hot oil through a fine jet under vacuum. Another claims complete deodorisation by allowing the oil, in a thin stream, to

flow down an inclined plane under vacuum at 100°–150° C.[26] High vacuum distillation permits the removal, not only of fatty acids, but of unpolymerised glycerides also. The residual stand oil has definite advantages over ordinary unprocessed stand oil, in that the tendency to develop cloudiness during storage, or after admixture with lead driers is absent, very low acidity is possible, and quicker drying and more tack-free films are obtained. Stand oils processed by the solvent extraction method have the disadvantage of the presence of traces of solvent, but with vacuum distilled oils this disadvantage does not exist. In spite of the many advantages of distilled stand oils they have not yet found for themselves a permanent place in the varnish warehouse probably because of their tendency to instability.

Deacidification with (*a*) *Basic Pigments.*—Deacidification of stand oils may be accomplished by mixing with basic zinc compounds such as zinc oxide or hydroxide, followed by filtration of the mixture after several days.[27]

(*b*) *Monoglycerides.*—Alternatively, the addition of the calculated amount (0·4 per cent) of linseed oil monoglycerides to a stand oil (A.V. 12) is effective in reducing the acid value to 5·3 after one hour's treatment at 260° C.[28] Glycerine and other alcohols are also effective alternatives.

Properties and Uses

There are many reasons for the use of stand oils in varnish manufacture. They confer good dry, quick set, controlled flow, durability, colour retention, and water resistance on varnishes containing them, in contrast to the effect of unpolymerised oils. They are particularly valuable in formulating finishes where minimum penetration of the surface is desired, and this is possible because of the increased size of their molecules. They require larger quantities of thinners to reduce them to workable viscosity and in consequence the resultant product is cheapened. They are, however, prone to certain defects unless care is taken. Stand oils with high acidity induce objectionable livering with basic pigments, especially with zinc oxide, and the acidity of stand oils used in paint and enamel media should be, therefore, carefully controlled. In order to give a balanced statement it should be noted that some workers claim that no correlation can be established between livering and acidity alone. Stand oils which have been excessively polymerised aid livering with basic pigments, and may cause "seediness" in varnishes made from them. Recent work indicates that livering is probably caused by a combination of acidity and degree of polymerisation. A mathematical equation for a limiting acid value and viscosity line has been derived for a bodied linseed oil, and beyond this, livering may be expected.[202] Skinning during storage is another trouble which may be encountered. Stand oils which are highly polymerised cause brushing difficulties especially in varnishes which are applied on large surfaces. It must be borne in mind also that stand oils are less soluble or miscible

than the parent oil and may need modified treatment. In the preparation of varnishes where a stand oil is to be used, especially if a "hard" type of synthetic resin is present, it is always advisable to mix the convenient minimum of stand oil with the resin at the maximum temperature, and after incorporation has been satisfactorily effected, the residual stand oil is added gradually, avoiding any serious reduction of temperature from the maximum. If the stand oil is added to the resin in excessive quantity initially, or too quickly subsequently, then precipitation may occur and it is often impossible to eliminate this condition even on prolonged heating. Before thinning the whole of the oil-resin mix it is advisable to check its solubility in a large excess of thinner (2 thinner to 1 oil-resin). If the solubility test does not remain clear on cooling, the heat treatment of the oil-resin mix should be prolonged.

Blown or Thickened Linseed Oil

Blown linseed oil is distinguished from stand oil by several characteristic properties. It ranges in colour from yellow to a deep orange, its specific gravity is higher, usually from 0·960–1·00 approximately, and it is less soluble in petroleum hydrocarbons. On heating blown oils during the preparation of varnishes, appreciable frothing occurs.

Blown oils are prepared by blowing air through the oil at an elevated temperature, generally below 150° C., and whilst the primary object of the process is to produce an oxidised oil some polymerisation occurs also. The oxidation yields oxy-acids and their anhydrides, as well as keto and oxy-keto acids.[29] The oil itself also becomes partly hydroxylated. Many methods have been suggested for the production of blown oils, and the following are typical. Linseed oil is blown at 70°–82° C. until a specific gravity of 1·00 is obtained; or linseed oil is first heated at 285°–327° C. until the iodine value falls to 130. The oil is then chilled to 132° C. and blowing is commenced. The temperature is allowed to fall to 93° C. and maintained until the iodine value falls to 85. Another method is to heat the oil rapidly to 315° C., cool immediately to 150° C. and blow with air to the desired viscosity.[30] Polymerisation may be prevented by the presence of maleic acid during blowing.[31] Contrary to general practice in the past, blowing of linseed oil at high temperatures has been used also. Considerable hydrolysis takes place and the resultant oil is highly acidic, unless special precautions are taken. Such oil is claimed to have excellent drying and wetting properties.[32] By blowing linseed oil at temperatures near 300° C., Blom [33] claims the resultant product to possess the properties of tung oil.

By reason of their partly oxidised condition blown oils generally dry more rapidly than stand oils. It has been suggested that in short oil varnishes their speed of dry is comparable with that of wood oil.[34] It is generally accepted that the presence of hydrophilic groups makes their water resistance poor,[35] but Stock [34] considers both this property

and acid and alkali resistance to be satisfactory when used in combination with rosin ester, copal ester, or rosin modified phenol formaldehyde resins. The durability of blown oil is problematic and it should be used in interior varnishes only.

Heavily blown linseed oil, produced at low temperature, reacts very easily with pure synthetic resins of the xylenol-formaldehyde type. This reactivity is greater even than that between wood oil and oil-reactive resins of similar type, so much so that with some proprietary brands of xylenol formaldehyde resin it is almost impossible to manipulate them on the works' scale without causing gelation. This unfortunate phenomenon can happen well below 150° C.

Vulcanised or Sulphurised Oil

Oils or fats containing unsaturated linkages absorb sulphur chloride with evolution of heat. This fact has been known for a long time and has been used as a means of measuring unsaturation.[36] Most varnish oils permit of vulcanisation with sulphur chloride and those commonly treated are linseed, perilla, and fish oils, and the corresponding blown varieties.

The best method is to add the sulphur chloride slowly to the oil with constant stirring and to avoid excessive temperature increase. Some protected processes add sulphur chloride in a solvent which is common also to the vulcanised oil. Governed by the type of product which is desired sulphur chloride up to 30 per cent. of the oil may be used. Useful oils may be obtained, however, by additions of as little as 2·5–3·0 per cent.[37] Blown oils tend to polymerise much more rapidly than unblown oils and the amount of sulphur chloride used in their treatment is correspondingly reduced. Oils are sometimes blown in the presence of sulphur chloride or treated with sulphur chloride (1 to 3 per cent) and blown subsequently.[38] Reactions involving sulphur chloride liberate hydrochloric acid and it is essential that this is removed before the vulcanised oil is used in paint media or varnishes. This may be accomplished effectively either by washing with water or by treatment with an alkaline substance such as lime.

Alternatively, oils may be treated with sulphur at temperatures above 100° C. Catalysts which aid vulcanisation are tetramethylthiuram disulphide or hydrogen sulphide.[39] Flowers of sulphur are the most convenient form to use, and the best method of incorporation is to sprinkle the sulphur slowly into the hot oil at the minimum temperature necessary for solution, with constant stirring. With heavily blown oils, unless the reaction is accomplished with minimum heat treatment, the product will gel. In every instance it is advisable to chill the vulcanised product rapidly and to thin out immediately.

The risk of gelation during sulphurisation can be reduced if the oil and sulphur are heated together in the presence of aniline diphenyl guanidine, diphenyl thiourea, or diethyl dithiocarbamate.

Sulphur treated oils tend to be darker in colour than oils obtained by sulphur chloride treatment at lower temperatures. Vulcanised oils are easily recognised by their characteristic odours. They are apt to gel on storage, particularly if the parent oil is a blown oil. Additions of sulphur to wood oil cause complete solidification during storage.

Vulcanised oils set rapidly when exposed as thin films, and it is this property which enables them to be used in the so-called wet-on-wet process. In this process several coats of pigmented oil are applied at short intervals, as soon as the preceding coat has set, and the resultant thick composite film hardens through subsequently. Vulcanised oils form the basis of many stoving finishes for rubber. The vulcanisation of oil endows it with good rust-proofing properties, low water resistance, and good durability.[40]

Chemically Treated Oils

In addition to the treatment of drying oils by sulphur or sulphur chloride, other methods of chemical treatment have been used. Solutions of drying oils in chlorinated hydrocarbons (e.g. ethylene dichloride), are treated with aluminium trichloride or boron trifluoride at 100° C. to produce polymerised products. Silicon tetrachloride and titanic chloride have a similar polymerising effect upon solutions of oil in suitable solvents. The polymerisation of unsaturated oils by means of tin chloride has been examined also. Oils with improved drying properties are claimed, by the treatment of raw, polymerised, or blown oils with solutions of phosphorus trichloride or phosphorus pentachloride in white spirit.[41]

Linseed Oil Substitutes

Lack of supplies of linseed oil and other drying oils has led German varnish makers to use a substitute known as El Firnis. Rossmann describes the mixture as having both the colour and viscosity of linseed oil, but it dries harder and more rapidly, and has better resistance to yellowing and moisture. According to Brückel[42] its composition is: linseed stand oil 21, rosin ester 12, alkyd resin 16, benzoline 50, and drier 1.

Tall oil and certain petroleum extracts have also attracted considerable attention as possible substitutes for drying oils.

Tung Oil

Source.—The Chinese oil is derived from the nuts of *Aleurites fordii* or *Aleurites montana*. The Japanese variety is obtained from *Aleurites cordata*, which is also known sometimes as abrasin oil.* The Chinese variety, *Aleuritis fordii*, is now also being cultivated extensively in Japan, and is said to be indistinguishable from the Chinese oil. China and the contiguous countries are the primary sources of supply, but smaller quantities are produced in many other parts of the world, including

* There is some confusion as to which species of *Aleurites* the description "Abrasin Oil" applies. The name has been given to *A. montana* also, but Sward has suggested that Mu oil is a better name for this variety.

South Africa, Kenya, Australia, New Zealand, United States of America (Gulf States), Brazil, French Morocco, India (Bihar, Orissa and Assam), Argentine, Dutch East Indies (Java), Malaya, Ceylon and British Honduras. In a review of the domestic tung oil industry in the United States of America in 1939, it was stated that there were already about 100,000 acres of tung oil groves in existence producing about 600 lb. of oil per acre.[203] The groves are increasing rapidly in area in a narrow coastal bent around the Gulf of Mexico. The results of growing tung trees on the Cameron Highlands (Malaya) have been disappointing, especially with the *Aleurites fordii*, although *A. montana* was more promising. In general, the climate was considered unsuitable, and fruit yields were uneconomically low.[207] Tung oil has been grown recently in Nyasaland and increases in production are expected in the future. The results were better with *A. montana* than *fordii*.

The oil from *A. fordii* grown in New South Wales varies in properties from different plantations, but on the whole the product is considered satisfactory.[230] Many of the tung oils derived from other than Chinese sources have comparable properties to the Chinese oil. The oils from French Morocco, India, United States of America, Java, Ceylon and British Honduras have been described as satisfactory substitutes.[43] Tung oil from other sources, if not of equal quality to the Chinese variety, could be substituted for it in an emergency without fundamentally affecting the properties of the final varnish.

Composition.—The approximate percentage composition of tung oil fatty acids is

	Per cent
Saturated acids	2·7– 5·4
Oleic or other unsaturated acids	14·3–18·6
Elaeostearic acid	76·6–80·4

The oil is obtained from the kernels of the nuts or fruits by expression. *Aleurites fordii* provides the majority of the oil of commerce and it is believed to contain a greater amount of elaeostearic acid than oil from *Aleurites montana*. There is, however, no marked difference between varnishes made with these two oils in respect of gloss, durability and water absorption.[44]

Properties

Smell.—Tung oil has a characteristic smell which is often easily detected, even after cooking, in a drying film of varnish. No method of permanent deodorisation has been discovered, although temporary deodorisation has been effected by passing superheated steam, carbon dioxide, or air under reduced pressure through the hot oil. Moisture in the presence of sunlight or air apparently produces the smell.[45]

Condition.—Tung oil appears on the market as a slightly viscous oil which sets to a soft paste at low temperatures. It is advantageous therefore to store the oil in tanks which can be heated by steam coils during spells of cold weather.

Varnish Constituents

Dry, Water Resistance and Webbing.—The characteristic properties which have made this oil so valuable in modern varnish manufacture are its unique speed of dry and its excellent water resistance. In carefully formulated varnishes it has outstanding durability. Unlike most other drying oils carefully controlled preliminary heat treatment is essential for good results. Raw wood oil dries matt and webs or crystallises at the slightest provocation. It is this defect which has to be eradicated by heat treatment.

Heat Treatment.—The heat treatment of tung oil is still a controversial subject. Controversy reigns as to the optimum temperature for immunity from webbing with maximum durability. Fonrobert [46] bases his treatment on the foundation that ordinary tung oil consists chiefly of α-elaeostearic triglyceride and that it is this modification which possesses the properties essential to a good varnish. Heat treatment stimulates a change from the α to the β form. Rapid heating to 280° C. with immediate cooling yields an oil with maximum polymerisation and minimum isomeric change. At lower temperatures, longer times are necessary to obtain adequate polymerisation, and the tendency of isomeric change is greater. Moreover, it is more difficult to eliminate webbing at lower temperatures. The durability of a tung oil film is said to be inferior if the oil is cooked below 270° C.[46, 47] Other workers, however, have modified these contentions.

Heat treatment of tung oil at high temperatures is a skilful procedure, partly because of the speed of polymerisation and partly because the polymerisation is exothermic; the heat generated being proportional to the temperature up to 320° C.[48] It has been demonstrated that tung oil requires less time than linseed oil to attain a given temperature, and requires more time to cool.[46] High temperature treatment (280°–300° C.) is known as the American method. Low temperature treatment (200°–260° C.) is described as the European or Continental method. It is obvious that the latter gives the greater margin of control.

Storage

Tung oil is one of the most expensive oils which the varnish maker uses, but restrictions on its use during the war have shown that it can be stored for long periods, up to several years, without detriment or loss of value. This is equally true of liquefied oiticica oils. The best storage conditions are that the tank is filled and sealed, all moisture excluded, and a uniform temperature maintained.[246]

Tung Oil Stand Oils

Straight tung oil stand oils are rarely used in varnish manufacture. It is more convenient to polymerise the oil during the initial stages of the varnish-making process, before the addition of the resin which may be used as a "chill-back," or to polymerise the oil in the presence of the resin. Little time is saved in preparing large quantities of stand oil since the time necessary for polymerisation is short, and, in addition,

a stricter control is possible if the polymerisation is delayed until the varnish is made. With certain types of synthetic resin it is essential that the tung oil is bodied in the presence of the resin.

If a low temperature stand oil is desired the process is easy to control. At 200° C. several hours' treatment is necessary. At 280° C. satisfactory polymerisation is effected in about ten to twelve minutes, but the actual time at 280° C. will be governed partly by the time taken to heat from 240° C. Unless special plant is available the best method for high temperature stand oils is as follows. Small batches of oil of about 10 to 20 gallons each should be raised as rapidly as possible to within 10° C. of the maximum polymerising temperature and removed from the source of heat. The temperature will rise to the desired extent and will probably remain thus until polymerisation is complete. Two to four gallons of raw tung oil should then be added to chill the bulk quickly, which may be cooled further, if necessary, by hosing down with water. The mixture of polymerised and raw oil thus produced can be used to chill subsequent batches. These will contain less raw oil. Many plants have been suggested whose function is to heat the oil rapidly to a high temperature for a short time followed by an equally rapid cooling. With such plants risk of gelation is eliminated.

One protected method is to heat tung oil quickly to 285° C., to transfer to another vessel maintained at 285° C. until polymerisation is complete and to cool suddenly. Another describes the passage of tung oil through a spiral at 315°–330° C., the bottom of which is cooled to prevent gelation. It has been claimed that a satisfactory stand oil is made by heating tung oil at 150° C. in the presence of ozone.[49] Boric acid is added to tung oil and the mixture heated to 260° C. Cooling is allowed to proceed slowly until the desired viscosity is obtained, and further polymerisation is checked by rapid cooling.[50] Another method is to polymerise the tung oil in the presence of a high boiling solvent which is subsequently removed. It can also be polymerised at a low temperature (105° C.), into a product suitable for varnishes, in the presence of 5–10 per cent of diethyl sulphate, which is dissolved in the oil. The treatment is interesting but diethyl sulphate is not a particularly pleasant material for use in the ordinary varnish factory. If an oxidised tung oil is required, the oil may be diluted with castor oil and oxidised below 120° C. When the treatment is discontinued the castor oil is removed by extracting with alcohol.[51]

If the temperature of tung oil is raised quickly in excess of 310° C., e.g. 330° C., and maintained for some time, decomposition occurs, gelation is delayed, and the product exhibits poor drying properties. It is believed that the poor drying and polymerising properties of overheated tung oil are caused by the formation of non-polymerisable cyclic compounds. Nevertheless it has been suggested that stand oils can be made by heating the raw oil to 360° C. quickly, maintaining this temperature for about fifteen minutes, followed by sudden cooling.[52]

Varnish Constituents

Tatimori has reported the results of work on the effects of a number of varnish constituents on the gelation of tung oil. Paraffin waxes, hydrocarbon oils, butyl stearate, triacetin, tricresyl phosphate, α-naphthylamine, hydroquinone and β-naphthol have a slight retarding effect on the speed of gelation. This is probably because they act as inert diluents. Certain organic acids, benzoic, cinnamic, and malic, have a pronounced retarding effect, and this, in the experience of the author, is equally true of maleic anhydride. This particular acid does induce polymerisation initially because of actual chemical reaction, but retards it subsequently. Other acids such as succinic and citric accelerate gelation as does also pyrogallol and α-naphthol, although the effect of the last named depends upon the amount present. When it exceeds 10 per cent it acts as a retarder. This reversal of effect is true also of ordinary and blown asphaltums, petroleum bitumens, gilsonite, stearine and coal tar pitches, and mineral rubber. Acceleration occurs when they are present up to 10 per cent but beyond this gelation is retarded.[223]

Liquefaction of Tung Oil Gels

Although accurate control has almost eliminated losses through gelation, the possibility of liquefaction of gels has attracted a good deal of attention in the past. If gelation has proceeded so that the oil has become a sticky semi-solid mass, liquefaction is difficult. If the polymerisation is arrested before this stage the chances of success are good. The highly polymerised oil can be heated with acidic peptising agents such as rosin, or masticated with glycerol and heated subsequently. Simultaneous additions of rosin and glycerol with heating have been suggested also. Ruff recommends heating the gel with varnish foots to 100° C. It is essential that the foots contain a large proportion of the lead soaps of linseed oil if they are to be effective. Alternatively, the lead soaps may be prepared by heating linseed oil with an excess of litharge. The addition of acetone causes their precipitation and they may be used by mixing with the tung oil gel in a neutral liquid, and heating at 100° C.[53] If the temperature of the gel is approximately 240°–260° C., but preferably nearer 260° C., finely divided litharge sprinkled on the surface will sometimes cause liquefaction. In order to obtain a more rapid reaction the litharge should be ground into refined linseed oil to provide a concentrated mixture, and this can be slowly poured on to the surface of the gel. Lead acetate has a similar peptising action to litharge.

Monoglycerides are claimed to be especially effective in inducing liquefaction.

Sudden and vigorous heating of tung oil gel causes partial liquefaction into a usable product, but the method, although practical in the laboratory, cannot be recommended as a commercial proposition.

The disposal of a reclaimed tung oil gel is a serious problem. Its highly polymerised condition and the presence of substances used to

aid liquefaction make it unsuitable for admixture with good grade varnishes. It can be mixed with varnish foots, which at periods find a ready market, used as a binding medium for putty, or when mixed with linseed oil used as a cheap paint medium.

Tung Oil—Linseed Oil Stand Oils

Mixed stand oils produced by the simultaneous treatment of tung oil and other drying oils provide useful varnish-making oils or media for good class paints. The mode of preparation has been studied in detail by Fonrobert,[46] and is controlled largely by the ratio of tung oil to the other oil. With one part of tung oil to two or three parts of varnish linseed oil ester interchange occurs, resulting in the formation of mono elaeostearic acid-di-linseed oil acid triglyceride. This type of oil is generally satisfactory, being easy to produce with little risk of gelation, and freedom from webbing tendencies. Fonrobert and others [54] prefer stand oils in which the two oils have been prepared separately, when good exterior durability is desired. It has been stated that when more than one part of tung oil is used with two parts of linseed oil there is insufficient linseed oil to permit complete ester interchange, as suggested above, and free tung oil remains. The free tung oil is thus believed to form highly polymerised and sometimes gelled agglomerates, scattered in a lightly bodied oil. In these circumstances it is best to heat tung oil and linseed stand oil to 280° C. Alternatively the presence of large amounts of tung oil might result in the production of triglycerides with more than one elaeostearic radical. Unfortunately there is very little published evidence on the type of reaction involved; but the alternative reaction should be borne in mind. When equal parts of tung oil and linseed oil are required the preferable method is to heat the tung oil alone in the normal way and to check with linseed stand oil. The effect of linseed oil upon the speed of polymerisation of tung oil becomes more apparent as the temperature and the proportion of linseed oil increases.[48]

Blown Tung Oil

Blown tung oils can be made but they do not possess any valuable outstanding properties and hence are rarely encountered. Their chief uses are in crystallising lacquers and matt finishes.

Perilla Oil

Source.—Perilla oil is obtained from the seed of *Perilla Ocymoides*, or *Perilla Nankinensis* and is produced exclusively in Japan, Manchuria, Northern India and the East Indies. *Perilla Ocymoides* has been grown successfully in Burma also. Experimental plantings in the U.S.A. have not, so far, proved successful.

Varnish Constituents

Composition.—The approximate percentage composition of its fatty acids is

	Per cent
Saturated acids	3·5– 7·6
Oleic acid	3·9–13·8
Linoleic acid	33·6–59·4
Linolenic acid	23·3–49·0

Properties

Its iodine value, which is reported as varying from 193 to 206, is exceptionally high for a drying oil. Although its iodine value has no doubt stimulated interest in this oil, no unanimity of opinion exists concerning its drying power in relation to similar oils such as linseed. Fryer and Weston, Tchang and Ling,[55] and Lewkowitch have found that perilla oil dries more slowly than linseed oil, but the majority of workers [56] have recognised its superior drying properties. With driers the times of drying of perilla and linseed oil are 3·2 hours and 5·6 hours respectively. Without driers the times are forty hours and seventy hours. Perilla oil has been suggested as an addition to poor drying linseed oils with the object of overcoming their defects.[57] Although irregular drying results have been obtained with raw or refined perilla oil, by comparison with linseed oil, there is no doubt that perilla stand oils are superior in drying properties to the corresponding linseed stand oils. Tchang and Ling (*loc. cit.*) confirm that the dry of perilla oil can be improved by two or three hours heating at 190°–200° C.

Like linseed oil, raw perilla oil has a tendency to break on heating. Perilla oil suitable for production of stand oil is produced by coagulating the "break" by heating, allowing to settle, and removing the mucilaginous matter by filtration. Statements have been made that perilla oil does not break, but these do not conform with the author's experience. The raw oil may be refined also by alkali treatment. Refined perilla oil is converted to stand oil readily by several hours' treatment at 300° C. The speed of polymerisation is noticeably greater than that of linseed oil.

Perilla oil has a distinctive pleasant smell which is accentuated on heating. The stand oils do not retain this smell. Since the oil has a lower flash-point than linseed oil (probably due to the presence of perillic aldehyde) extra care should be taken during varnish or stand oil manufacture. Comparative figures (C.F. Pt.) for linseed and perilla oil have been given as 282° and 215° C. respectively.[58]

Blown perilla oils do not exhibit the outstanding drying properties which might be anticipated.

In the recent search for tung oil substitutes, perilla oil has received its due share of attention. Whilst it cannot be regarded, in any way, as a substitute for tung oil, for most of its properties lie between those of linseed and tung oil, it is undoubtedly a better oil than linseed oil in many directions. A great future is predicted for it. The stand oil has better gloss and exterior durability and is more resistant to ingress of

moisture. In stoving finishes it dries tougher than linseed oil and yields films with excellent surface hardness. It provides better printing ink media than linseed oil. Its chief defects are, that it demonstrates an increased tendency to yellow both on stoving and on exposure: it tends to surface dry, and this betrays itself as rivelling during stoving, and stoved films lack flexibility. Unpolymerised oil exhibits an inclination to "crawl" but this may be eliminated either by heating, or by the addition of 0·01 per cent of benzene-azo-benzene-azo-β-naphthol.[59] Perilla oil tends to bloom rather more than linseed oil.

Oiticica Oil

Source and Composition.—Oiticica oil is obtained from the seeds of *Licania rigida benth.*, indigenous to Brazil. The approximate percentage composition of its fatty acids has been given as

	Per cent
Saturated acids	11·3
Oleic acid	6·2
Licanic acid	82·5

The oil is obtained either by expression or by solvent extraction.

Properties and Uses

When first expressed it is quite liquid but sets to a soft pasty mass on storage. This is a phenomenon which is governed chiefly by temperature only. If the oil is obtained by hot extraction methods it is said to remain liquid for long periods without showing signs of solidification. Special treatment involving high temperatures is said to eradicate permanently the tendency to solidify.

Oiticica oil in the paste form is inconvenient and unsuitable for the varnish maker. Much time is wasted in weighing when measuring would suffice, and in transference. In this condition, too, oxidation is liable to occur and this results in the production of gelled particles which do not disperse on heating. These persist even in the finished varnish and necessitate removal by filtration or centrifuging when perhaps neither of these two processes would be used in the normal way. In addition, appreciable darkening occurs on heating and comparative experiments have shown, that using paste oiticica oil, it is impossible to produce varnishes as pale as those from wood oil. The danger of spontaneous ignition also exists. Half-filled barrels of paste oiticica oil have been known to char badly and ignite. Kappelmeier has reported the tendency of the oil to gel even at normal temperatures, and its gradual decomposition on long storage.[60] If the oil is stored in a tank maintained at 35° C. or over it remains in a liquid condition. Or since the oil is likely to be used in a bodied condition ultimately, it may be convenient to convert a new consignment of oil immediately to a light stand oil, and this is accomplished by heating at 225° C. for about

forty-five minutes. Usually this will remain liquid on storage, but sometimes a voluminous greenish precipitate settles out. Treatment at temperatures as low as 100° C. for thirty minutes will delay subsequent re-solidification. It is obvious that heat treatment at, or immediately after, expression is the best means of preventing the aforementioned difficulties. Much oil is now preheated before it is supplied to consumers.

Raw oiticica oil behaves similarly to tung oil on drying. It shows a marked tendency to web and frost but it is not so susceptible to influences inducing these defects as tung oil. It is essential that the oil is polymerised to obtain the best results from it, and while it polymerises rapidly on heating it is easy to control. To eradicate completely its frosting tendencies heat treatment in the presence of resins is necessary. This trouble is claimed to be removed also by heat treatment in excess of 150° C. and assisted by the presence of boron trifluoride (0·05–0·5 per cent).[251] Compared with tung oil it requires approximately twice the duration of heating over the temperature range 250°–300° C.[61] When mixed with resins the differences in the speeds of polymerisation are even more marked. As with tung oil the best temperatures for treatment are in excess of 280° C., and a few minutes at this temperature followed by sudden chilling suffices for the production of satisfactory stand oils. Kemner, however, states that the oil should be heated at 250° C. for optimum properties.[62] It is interesting to note that Stock [63] states that stand oil heated at 250° C. for half an hour has inferior durability to the raw oil. A method for producing bodied oiticica oil, which is reminiscent of a method advocated several years ago for similar treatment of tung oil, is to pass the oil through a heated coil. A monel metal coil is used in a lead-antimony bath.[213]

Oiticica oil dries more rapidly than any other natural varnish oil with the exception of tung oil. The chemical and water resistance of oiticica oil are good but inferior to those of tung oil. The oil has a pronounced tendency to develop turbidity, in varnishes which have been prepared by the addition whilst hot of driers such as litharge, manganese dioxide, etc. Moreover, the addition of litharge at 270°–280° C. is not practical, due to excessive frothing.[64] It is preferable to add driers in the form of easily soluble salts at the minimum temperatures possible, or as naphthenates, resinates or linoleates in the form of terebines. Excess of lead drier should be avoided in deference to the pronounced inclination of oiticica oil to develop turbidity with it during storage. Oiticica varnishes do not skin so readily as those from tung oil.

The indiscriminate inclusion of oiticica oil in all types of varnishes has led to conflicting reports on its durability. Although some workers have advocated it as a general substitute for other oils [46, 65] it is now quite apparent that its valuable properties must be exploited in carefully selected directions only, if troubles are to be avoided.

Oiticica oil films suffer from embrittlement on ageing, and with ester gum or copal in particular, premature breakdown results. With ester

gum, durability and gloss retention are said to be inversely proportional to the amount of oil used,[66] but the results vary considerably with the cooking conditions. If the cooking temperature is kept below 238° C. good results are obtained. With phenol formaldehyde resins, on the other hand, varnishes with excellent durability, at least equal to that with tung oil, are possible. Other workers have confirmed that oiticica oil is best used with phenol formaldehyde or modified phenol formaldehyde resins.[67] The speed of polymerisation of phenol formaldehyde resins with oiticica oil is greater than with tung oil and this is thought to be due to the presence of the keto groups of the licanic acid. *p*-Alkyl phenols in the presence of phosphoric acid react with the keto group of the oil to yield satisfactory varnishes. The embrittlement of oiticica oil in exterior varnishes can be modified by the addition of a plasticising oil like soya bean oil. Any checking and livering tendency of oiticica oil is claimed to be prevented by cooking the oil during the preparation of the stand oil, with a few per cent. of ordinary castor oil.[241] Mundy[68] advances the opinion that where oiticica oil and linseed oil are present in the ratio of more than two of linseed to one of oiticica oil, then the chief properties of the mixture, including durability, will be equal to that of a corresponding tung oil mixture.

Soya Bean Oil

Source and Composition.—The oil is obtained from the beans of Glycine or Soya hispida, indigenous to China, Japan and Manchuria. Some oil is produced in the United States of America, Russia, Yugoslavia and other parts of Europe, and a little from experimental sources in Great Britain. Growing trials have also been conducted in New Zealand. The approximate percentage composition of its fatty acids is

	Per cent
Saturated acids	11·5–14·3
Oleic acid	25·9–33·7
Linoleic acid	52·0–58·8
Linolenic acid	2·1– 5·8

The oil is removed from the beans by pressing or by solvent extraction.

Information has been given on the acid and alkali refining of this oil, and the final conclusions are that best results are obtained using dilute sulphuric acid (1 per cent), followed by washing with alkali in 50 per cent excess. Alkali refining results in appreciable losses of oil, which increase in proportion to the concentration and excess of alkali, but the colour of the oil remains practically unaffected.[248]

The iodine value of the oil obtained from the soya bean is influenced by the conditions of cultivation. Ripening causes a gradual increase in iodine value, but the ultimate value is determined chiefly by the prevailing temperature.[249]

Properties and Uses

Some oils tend to " break " on heating and should be tested before use.

Soya bean oil is not used in very large quantities in varnishes in Great Britain but indications demonstrate that it is becoming more popular in the United States of America. Its drying properties are much inferior to those of linseed oil, but in spite of this it is a useful oil for special purposes. Linseed oil dries in about one-third the time required by soya bean oil.[69] Attempts have been made to improve its drying properties by the removal of antioxidants. Phosphatides among other substances have been recognised as possible retardants.[70] Treatment with acid or alkali is claimed to destroy antioxidants, as well as treatment with oxidising agents like potassium permanganate or dichromate. The following figures represent the improvements effected :

	Drying time
Raw soya bean oil	150–160 hours
Raw linseed oil	34 hours
Alkali refined soya bean oil	8 hours
Soya bean oil after treatment with potassium dichromate	23 hours

Unlike most other drying or semi-drying oils used in varnish manufacture, it has been said of soya bean oil, that, in the absence of driers the drying films never increase in weight beyond their original weight at any state of the oxidation. This is a very striking assertion and for this reason it is perhaps advisable to await further confirmatory evidence.[205] While Ware [71] agrees that acid or mild pre-oxidation treatment improves the speed of dry, he states that it is still inferior to that of linseed oil. Blowing of a stand oil is claimed to improve the drying properties.[72] Excessive additions of drier are not advocated. Like linseed oil, soya bean oil bleaches on heating. Its speed of polymerisation is, however, very slow and requires about four times the time at 300° C. Mixed stand oils of soya bean with other oils form useful combinations for varnishes. Co-polymerisation of two parts of perilla and one part of soya bean oil yield an oil equal in drying properties to a corresponding linseed stand oil. The ester interchange occurring during the process is essential, since simple mechanical mixtures of perilla stand oil and soya bean stand oil do not exhibit the same drying properties.[73] A mixed stand oil of soya bean and tung oil, which is said to be free from the defects of either oil, is made by heating the mixed oils to an exceptionally high temperature (455° C.), for a short time in a tube with rapid cooling.[74]

In paint media, small additions of soya bean oil (15–20 per cent) can be made without seriously affecting the dry but to improve the flexibility. With perilla oil mixtures larger additions are possible. Small additions of the oil to tung oil or oiticica varnishes which tend to become exceptionally brittle on exposure, will minimise this tendency

and improve the durability without hindering other properties seriously. Quite durable paints can be made from ordinary soya bean oil.

Soya bean oil has outstanding colour retention both on exposure and stoving. For this reason it is included in air drying and stoving white enamels and in alkyd resins.

Fish Oils

Source.—There are many varieties of fish oil on the market derived from two sources: Oils from marine animals and ordinary fish oils. The sources for the former oils are whales (*Balaena*), worked up in America, Norway, Iceland, Japan and the Lofoden Islands; seals (*Phoca*); dolphins and porpoises, walruses, etc. The chief sources for ordinary fish oils are menhaden fish (*Alosa menhaden*), worked up chiefly in America; Japanese sardines (*Clupanodon melanosticta*) and Japanese herrings (*Clupea pallasi*), worked up in Japan; North Sea herrings (*Clupea harengus*), treated in Norway; and pilchards.

Composition.—The composition of fish oils is very complex, but they consist of mixtures of both highly unsaturated and saturated fatty acids in the form of glycerides. According to Reizinstein [75] crude fish oils contain

	Per cent
Myristic acid	6
Palmitic acid	12–14
Stearic acid	2– 4
Palmitoleic acid	14–16
Oleic acid, Linoleic, Linolenic acid	30
Clupanodonic acid	18
Therapic acid, Jecoric acid	the residue

Traces of octadecatrienoic acid have been discovered also.[111]

Antarctic seal oil has been found to contain acids of the following types: substantial amounts of highly unsaturated acids like clupanodonic, scoliodonic and nisinic, acids which are less unsaturated like oleic, and the usual saturated acids—palmitic, stearic and myristic.[215]

Production.—Of the sea animal oils, whale oil has become the most important for the varnish trade. Whale blubber is boiled with steam at ordinary or higher pressures to obtain the oil. Of the ordinary fish oils, sardine, menhaden, herring and pilchard oils are the most important. The fish are generally boiled with water and the oil is skimmed off; treated with steam to separate the oil; or allowed to rot when the oil is obtained by expression.

The latest method of obtaining oil from menhaden is based on steam treatment in which the menhaden are steamed and pressed. The mixture of fish oil and water is then first roughly screened to remove suspended solids, and then sent through a vibrating screen *en route* to a centrifugal slime separator. The oil, water, and wet solid matter are thereby separated. The fish oil, which may still be contaminated with a little

water, is finally freed of this by centrifuging, and a product of improved properties including a more pleasant smell is obtained.[214]

The oils appearing on the market vary considerably in quality as reflected in intensity of objectionable smell, in colour, in speed of dry, and in freedom from separated matter. Bulk deliveries of sardine oil, for example, may contain large pieces of fish.

Crude fish oils are of little value to the varnish or paint maker. They dry more slowly than linseed oil and do not harden to the same degree ultimately. Although fish oils are not used to a great extent in varnish manufacture, recent years have seen a large volume of experimental work conducted with the object of eradicating their defects. It is accepted generally that it is the presence of saturated acids, and glycerides such as stearine, which contribute to the film defects, including inferior dry. These are sometimes removed by chilling. The cooling and subsequent filtration of whale oil results in an improvement in iodine value from 90–120 with a simultaneous improvement in dry. By chilling sardine oil and removing the solid saturated triglycerides, an oil with an iodine value of 200 was obtained.[76] From pilchard oil the saturated constituents are removed by steam distillation, and the film of the improved oil is said to be superior to that of other drying oils for freedom from blooming and yellowing, and for gloss, hardness and water resistance.[77] Untreated oil is inferior to linseed oil for hardness and water resistance.

Mucilaginous matter can be removed from fish oils by the addition of 0·5 per cent of oak bark extract.[78] Another method of refining fish oils, which is especially applicable to sardine oil, is to treat the oil with an organic basic compound, wash away the soapy material, and then wash finally with dilute acid. Ethanolamine is suggested as a suitable basic material, and although it may be effective it seems to be an expensive reagent to use, unless the resultant soaps can be worked up for suitable markets.[204]

Properties and Uses

Much contradictory work has been published on the merits and defects of fish oils. With reference to Japanese sardine oil, Erastova and Roganova state that however the oil is refined it is inferior to linseed oil.[79] Films of fish oil become tacky on exposure, especially when the humidity is high, and Ohl has found them to have poor water resistance and durability.[80] In contradistinction Hignard claims impermeability and very good durability, especially in sea air.[81] It is generally agreed that fish oils give soft flexible films which bloom and yellow badly. The film strength of fish oils, even the stand oils, is noticeably inferior to that of linseed oil. Fish oils are peculiar in their property of resistance to decomposition by heat, and for this reason they have been suggested as the basis for paints and varnishes which are subjected to high temperatures.[80, 81]

Fish oils processed by heat treatment or blowing are undoubtedly superior from a varnish-making standpoint than the unprocessed oil.[82] In the production of stand oils excessive overheating should be avoided since this is said to cause decomposition or molecular rearrangement. The maximum temperature should not exceed 280°–295° C.,[83] and three to four hours should suffice to provide a useful stand oil. The speed of polymerisation is governed to some extent by the stearine content of the oil. Fish oil stand oils are dark in comparison with similar stand oils from other drying oils, although the extent of the darkening can be controlled by using stainless steel or aluminium pots. An atmosphere of carbon dioxide or, alternatively, a low pressure are advantageous. The removal of saturated ingredients and unpolymerised oil from the stand oil by high vacuum distillation is another refinement aiding in the production of an improved oil.[84]

Blown fish oils are more valuable than heat polymerised oils.[85] Much of their objectionable odour disappears either on heating to 260° C. or on blowing.[75] Temperatures of 120° C. or 200°–250° C. have been used for blowing. Blown fish oils are claimed to be soluble in mineral spirits without separation [75] but they have gelling tendencies during storage.[86]

When it is desired to improve the flexibility of other oil films fish oil may be blended with perilla, oiticica or tung oil, and it is in such blended oils that it will be found most valuable. Oxidised or polymerised seal oil, in admixture with linseed or other oils, has given good paint media from the point of view of durability, but the mixtures possess the disadvantage of slow drying properties.[208] A paint oil, covered by British Standard Specification 925, is satisfied by a 15 poise stand oil prepared from three parts of linseed to one part of fish oil.

Fish oils (sardine oil) react with phenolic resins to a greater extent than linseed oil, and a reaction between pilchard oil and phenol has been studied by Riddell.[87] The reaction product was found to be toxic to pile or ship's worms.

Haco Oil

This is an oil which has attained some popularity in Germany recently. It is believed to contain acids isomeric with linolenic and elaeostearic acids, together with acids possessing four or five double bonds. It is, in fact, a specially processed whale oil, free from smell, yielding a film harder than that of linseed oil. For underwater paints it is claimed to be superior to tung oil.[88]

Dehydrated or Dehydroxylated Castor Oil

Source.—Castor oil is derived from the seeds of *Ricinus communis* which is grown in many parts of the world, including India, China, Manchukuo, South America (Brazil), South Africa, United States of America, Java, Mexico, French Colonial Africa (Algeria), Russia and

countries bordering the Mediterranean including Yugoslavia. The oil is separated by extraction or expression. Albuminous material is coagulated by steam and filtered out. Recent work in India has shown that industrial alcohol is an eminently suitable solvent for extraction of the oil from the seed, when the alcohol is available and cheap. The alcoholic solution of the oil is diluted with water to separate the oil, which is yielded to an extent of 4 per cent more than by the normal treatment. A further advantage of this treatment is that the whole of the oil obtained is in a pure condition.[206]

The solubility of castor oil in ethyl alcohol distinguishes it from all the usual vegetable oils, which are insoluble.

Composition of Castor Oil.—The composition of the fatty acids is as follows :—

	Per cent
Stearic acid	0·3
Dihydroxystearic acid	1·1
Oleic acid	7·2
Linoleic acid	3·6
Ricinoleic acid	87·8

Dehydration of Castor Oil

Castor oil is a non-drying oil and thus is of little value except as a plasticiser.

Castor oil which has been subjected to chemical or heat treatment, on the other hand, provides a useful varnish oil. Whatever treatment is used the object is to increase the number of unsaturated bonds from one to two. This may be accomplished in two ways: either by direct dehydration of the oil, or by dehydration of the fatty acids of castor oil with their subsequent re-esterification by glycerol. The latter method was used by Scheiber and has resulted in the "Synourin" type of drying oil.[89]

The direct dehydration of the oil has attracted considerable attention, probably because of its relative simplicity. This process is obviously much cheaper since it avoids hydrolysis of the oil and the final re-esterification. It is, moreover, a process which the ordinary varnish maker can control with good results, although it is claimed that the reaction does not normally proceed to the same extent as with fatty acids.[90] Barbot has thrown considerable light on the mechanism of the dehydration reactions.[139] Apart from the production of a triglyceride of increased unsaturation, and water, other possible reaction products obtained at higher temperatures include undecenoic, myristic, palmitic, stearic and oleic acids, heptaldehyde, acrolein, sebacic acid semi-aldehyde and octylene. To this list of dehydroxylation degradation products must be added, glycerol and oenanthol.

Contrary to early beliefs and some present claims, dehydration results in an oil in which the predominating fatty acid radical is 9 : 12 linoleic acid with its isolated unsaturated bonds. By comparison the amount

of the 9 : 11 acid present is very much smaller. This has been established by diene value measurements of Priest and Mikusch,[140] and its importance emphasised by Greaves [141] and Mundy.[142]

Many catalysts have been used to facilitate the dehydration reaction, since undue heating at elevated temperatures readily stimulates polymerisation and this, in the final product is not always desirable.

Using toluene sulphonyl chloride, castor oil may be dehydrated at 250° C. in vacuum, or at 270°–280° C. at ordinary pressure.[91] Oxides of metals have also been used successfully. Tin oxide has been used in a reaction requiring eight to twelve hours at 200°–250° C. and 5–20 mm. pressure. Dienol, a dehydrated oil produced in Switzerland, is believed to be produced in the presence of oxides such as those of tungsten, thorium or molybdenum, or of mixtures such as iron and zinc oxides with aluminium hydroxide.[143] According to Blom, dienol consists entirely of the conjugated acid, an object attained by conducting the dehydration in the presence of a salt of unstated composition.[97] Other workers claim to have prevented the formation of the 9 : 12 acid during dehydration also, but as indicated already the results of more recent work provide strongly opposing evidence.[96]

Other oxide catalysts include litharge, cobalt oxide, mixtures of zinc and aluminium oxides, and mixtures of litharge and manganese dioxides.[95]

Dehydration is claimed to occur at 140° C. in vacuum in the presence of bleaching earths,[92] and in this respect fuller's earth has been found to be effective although the product is rather dark in colour. Another process involves the heating at 280°–290° C. and ordinary pressure, in the presence of aluminium oxide and zinc.[93] China clay has also given good results.

Sulphuric acid and its derivatives exert a definite catalytic effect. Among the derivatives of sulphuric acid, the hydrogen sulphates of potassium, sodium and ammonium are effective but tend to give dark products. Potassium pyro-sulphate and sulphonated castor oil have been used at 190°–250° C. in the presence of carbon dioxide, nitrogen, or sulphur dioxide.[94] The use of methionic, ethionic, or methane disulphonic acids have been mentioned in other patents.[145] Good results are also claimed for phosphoric acid derivatives, and for a mixed catalyst of zinc ricinoleate and carbonate, for boryl pyrosulphite, and for boric acid.[257]

Another method of removing the hydroxyl group consists in first reacting it with a suitable organic acid, and subsequently decomposing the resultant ester by heating. Acids suitable for esterification are acetic and oxalic acids.[144]

Dehydration may be effected, either on the oil directly, on its fatty acids, or on solutions of either in a suitable solvent. With the latter method, it is, of course, essential to remove all traces of solvent from the finished product. A method involving the heat treatment of castor oil fatty acids, sulphuric acid, and glycerol, in which dehydration and esterification are said to proceed simultaneously, has been patented.[256]

Varnish Constituents

During dehydroxylation of castor oil and its subsequent bodying the acidity tends to rise substantially unless special precautions are taken to avoid it. Adjustments consist in introducing a small amount of ammonia or an ammonia-generating compound, e.g. ammonium oxalate, during the heat treatment, or alcohols such as glycols, glycerol, sorbitol, etc.[255]

Good reviews on the dehydration of castor oil have been given by Forbes and Neville,[146] Greaves,[141] Mundy,[142] and Morgan.[138]

Dehydroxylation of hydroxystearic triglyceride by heating with potassium persulphate at 250° C., yields a thin oil with good drying properties.[258]

Dehydrated Castor Oil Stand Oils

Stand oils may be prepared from dehydrated castor oil by heating at 260° C. or higher until the desired viscosity is attained. The acidity generally increases with the viscosity and may be as high as 20. The free acids, however, are said to be of a lower molecular weight than those which occur naturally in castor oil, and for this reason are claimed to be relatively free from a feeding tendency with basic pigments. Castor oil may be dehydrated in the presence of linseed oil at 240°–250° C. under vacuum to yield a mixed stand oil.[98] Mixed stand oils may be prepared by heating dehydrated castor oil and other drying oils (e.g. linseed, perilla) at 260°–300° C. Prolonged heating will cause gelation.

Properties and Uses

Dehydrated castor oil is an oil of unique qualities and some have claimed it as the ideal drying oil. It may be regarded, roughly, as intermediate in properties between linseed oil and tung oil. When drying it "sets off" quicker than linseed oil but tends to leave a surface tack which does not readily disappear. The dried film is more flexible than that of tung oil and is more durable than either linseed or tung oil. It has outstanding non-yellowing properties. Of the drying oils it holds pride of place for this property whether resistance to yellowing is required on exposure to light, to darkness, or on stoving.

Like tung oil, if insufficiently driered or cooked it shows a definite tendency to frost but this defect is easily eradicated. Its water resistance is superior to that of linseed oil, whilst its reactivity with 100 per cent phenol formaldehyde resins can be exploited to make good chemically resistant varnishes. An optimum cooking temperature of 315° C. is suggested.

Stoved films of dehydrated castor oil exhibit a marked tendency to rivel and have only mediocre strength. They need to be reinforced with other oils or resins to overcome these defects.

In decorative varnishes the oil can best be substituted for a mixture of linseed and tung oil.

Processed and Synthetic Drying Oils

In the last two or three years, the position of synthetic drying oils in the varnish trade has undergone substantial and far-reaching changes. Many of these new products are available in commercial quantities, but in contrast, Trienol seems to have slipped quietly away out of sight and almost out of recollection. Its disappearance may be the direct result of the European conflict, in which case it may re-appear on the market.

Improvements have been effected in drying oils in several different ways, but the products cannot always be regarded as truly synthetic in character. For convenience of consideration and to avoid confusion improved drying oils are sub-divided into two groups. The one includes oils produced chiefly by physical treatment, and these may be fairly described as processed oils; the other group includes oils which have been produced by chemical treatment involving a definite change in chemical structure of the fatty acid chains, or reaction of fatty acids with alcohols other than the natural glycerol. The latter group embraces what may best be described as the true synthetic oils.

The *processed oils* include those obtained by :

1. *Fractional Distillation of the Fatty Acids and Subsequent Re-esterification.*—Improved drying oils are obtained by fractional distillation of the fatty acids themselves, and the object is to segregate acids with varying degrees of unsaturation. The more unsaturated acids are then re-esterified. This procedure has been shown to be definitely a commercial proposition, and a fatty acid, known as Neofat 19,[177] is prepared from fatty acids from marine oils which are subjected to fractional steam distillation under vacuum. The low boiling saturated acids are, in this way, separated from the higher boiling unsaturated acids. Neofat 19 can be re-esterified with any suitable polyalcohol or used in the production of alkyds made by the fatty acid method.

Stingley is rather more explicit in the record of his own original research on the fractional distillation of the acids of marine oils, in that, he points out that it is the C_{20} and C_{22} acids which are separated and then esterified with glycerol. A rapid drying oil is obtained which, unfortunately, exhibits a tendency to brittleness on ageing. It is claimed to be equivalent to linseed-tung oil mixtures. A mixture of 35 per cent of this synthetic oil with 65 per cent of soya bean oil is similar in performance to linseed oil.[199]

2. *Molecular Distillation at High Vacua of the Vegetable Oils Themselves.*—This treatment has not been very successful, partly on account of expense, because extremely high vacua are necessary, and partly because of the difficulty of separating into convenient fractions the complex mixture of triglycerides present in the natural oils. Vacua of the order of 0·001 mm. of mercury are used, and the heating and distilling

surfaces are arranged to be very near each other. One cm. has been cited as a convenient distance of separation.

The process has been used with most success on the separation of stand oils into improved constituents.

Waterman and Oosterhof[25] succeeded in the molecular distillation of a 55 poise stand oil, into 32 per cent of unpolymerised distillate with a molecular weight of 757, and an undistilled residue with a high viscosity of 379 poises and a molecular weight of 3,460. Another worker claims to have separated ordinary linseed oil with an iodine value of 177·9 into fractions with iodine values varying from 148 to 190.[185] Oils with iodine values as low as 120 have been molecularly distilled, and the non-volatile residues have been converted into useful drying stand oils.[190] Fish oils have always presented drying problems to the varnish trade and it is not surprising, therefore, that their treatment by molecular distillation has formed the subject matter of several patents.

The reported results of molecular distillations on natural oils have not always been highly successful. Details are given of the distillation of large batches of soya bean and corn oil at an average pressure of 0·002 mm. Hg. With batches of 700–1000 gals., the rate of distillation was slow, being only 7–8 gals. per hour. No marked fractionation of the oils was achieved, but the process is valuable in that the unsaponifiable portion of the oil is removed in the first two fractions, and that most of the odorous and colouring matter is eliminated also.[198]

On the whole, however, some measure of success has been achieved, in obtaining oils of a higher degree of unsaturation from oils, which normally, as such, are regarded as insufficiently unsaturated or which possess insufficient drying properties for certain varnish making purposes.

3. *Solvent Extraction.*—Solvent extraction is practised on both natural and bodied fatty oils, although most of the success of the process has been achieved with the latter. The object is always to obtain better drying oils from the semi-drying kinds. Some idea of the effectiveness of fractional extraction of semi-drying oils can be obtained from the results of the work by Kleinsmith and Kraybill on soya bean oil, with the common alcohols and furfural. Furfuryl alcohol has also been suggested elsewhere as a suitable solvent. A fraction representing about 20 per cent of the original oil with an increase in iodine value of 6 per cent was produced.[195]

More encouraging results are reported by Bull and Wheeler who treated soya bean fatty acids with acetone in the approximate ratio of 30 parts of acetone to 1 part of acid. Fifty per cent of acids with an iodine value of 180 were separated by crystallisation at −50° C.[196] Fatty acids from menhaden mixed fatty acids, with an iodine value in excess of 235 were obtained by dissolution in 10 parts of solvent (hexane, petroleum ether, or amylene), followed by excessive cooling to −80° C. The saturated acids are precipitated.[197]

Light sardine oil stand oil (13 poises at 25° C.) is extracted with an alcohol-ketone mixture. The original oil is, in this way, divided into

roughly equal parts. The part with drying properties is sold under the name of Polymerol A.[178] Dehydrated castor oil stand oil is improved after solvent extraction, using ethyl alcohol.[194]

Solvents such as aniline, furfural, or polyethylene glycol, have also been used with fatty oils at such a temperature that two phases are maintained, but the temperature is not so low that solidification of the insoluble portion of the oil occurs. The more highly unsaturated triglycerides are extracted in this way.[191] The saturated triglycerides remain undissolved. Temperatures down to −20° C. are suggested.

In another process water is added to a solution of oil in furfural. Colouring matter, saturated constituents, and sterols are left in solution, whilst the unsaturated constituents are deposited.[179]

Some methods of solvent separation involve the use of two solvents —the one substantially non-polar and the other strongly polar. Patented methods for the separation of natural triglycerides have been based on this treatment, the oil being divided into two parts.[184]

Other processes involve fractional crystallisation after preliminary chemical treatment. By reason of the fact that fatty acids may be halogenated selectively, it is possible to segregate the halogenated acids by fractional crystallisation.[183]

Natural fatty oils are subjected to alcoholysis by treatment with monohydric alcohols, suitable alcohols being methyl, ethyl or propyl alcohol, so that the fatty acid esters contain less than three ester groups per molecule. Subsequent treatment of the products with furfural results in a segregation of more unsaturated esters, and these then made to undergo further hydrolysis with glycerol.[193]

The method of solvent extraction may be applied directly on materials such as seeds, etc., containing the oils. Furfural or furfuryl alcohol have been used for such extractions, and temperatures around 40° C. are used. When the oil has been extracted the solution is cooled, and this has the effect of separating the highly saturated glycerides as a liquid phase. The remainder is worked up to yield an improved oil.[225]

4. *Removal of anti-oxidants* in the naturally occurring oil by treatment with reagents like benzoyl peroxide.[149]

5. *Adsorption Separation of Glycerides.*—Natural triglycerides may be separated into portions by dissolving them in a suitable hydrocarbon, and passing the resultant solution through a column packed with adsorbent material. Alumina has proved satisfactory for this purpose, but there appears to be considerable practical difficulties to overcome in the dissection of the packed column into convenient fractions.[186]

6. *Electrical Treatment.*—Results on the voltolisation of linseed oil have been reported. The oil was subjected to 5,200 volts and a frequency of 800, in an ozoniser, under a soft vacuum, in the presence of air or nitrogen for about fourteen hours. The voltolised oil was found to dry appreciably quicker and harder than a stand oil bodied at 285° C. for fourteen hours, or an oil blown at 200° C. for thirty-two hours.[189]

The synthetic oils include those obtained by :—

1. *Removal of Hydroxyl Group as in the Conversion of Castor Oil into the Dehydrated Product.*—Dehydration or dehydroxylation may be effected either on the oil itself, or on its constituent fatty acids which are then subsequently esterified. Such oils have been described in detail already under Dehydrated Castor Oil.

2. *Removal of the Keto group from the licanic acid of oiticica oil* by means of various reagents. Some of the most promising reagents for this purpose are semi-carbazide and substituted semi-carbazides, but nothing of commercial value has been obtained so far by these means.[150]

3. *Isomerisation of Unsaturated but Non-conjugated Oils into the Conjugated Variety.*—This has been accomplished in several ways, some of which have proved to be sound commercial propositions.

Three types of isomerisation can occur, namely : structural, which involves movement of unsaturated bonds, atoms or groups of atoms ; geometrical ; and optical. Battline observes that oil isomerisation is nearly always structural with the possibility of some geometric, but that optical isomerisation has not, as yet, occupied much attention.[165]

(*a*) *Treatment of the Drying or Semi-drying Oil, or the Constituent Fatty Acids, with Alkaline Solutions at Elevated Temperatures.*—Induction of conjugation by means of alkali treatment is a very interesting phenomenon, but the process is costly in that after isomerisation has been effected on the fatty oil or its acids, the product has to be treated with mineral acid to liberate the isomerised acids from the alkali soap, and these in turn have to be re-esterified with a polyhydric alcohol.

Isomerisation can be effected with several different alkaline materials, and the hydroxides of sodium, potassium and lithium have been used successfully. Different solvents for the alkali modify the reaction, in that although the speed of reaction is greater with an alcoholic solvent for a given temperature, an aqueous reagent permits the use of a higher temperature than that possible with the lower alcohols. A high temperature is, of course, an important stimulator of saponifications. Ethylene glycol gives good results as higher boiling solvent, but by comparison with water and industrial alcohol it is expensive.[168]

Comparative isomerisation rates for the conversion of linolenic acid to pseudo elaeostearic acid (10, 12, 14-octadecatrienoic acid) in different solvents, as found by Kass and Burr (*loc. cit.*), are 7–25 days for aqueous-alcoholic potash, 6–24 hours for the butyl alcoholic reagent, and ½–2 hours for the ethylene glycol reagent.

The work of Bradley and Richardson in 1942,[166] following on the earlier researches of Dann and Moore,[167] has revealed the possibilities of isomerisation by saponification. Bradley and Richardson treated the fatty acids of linseed, soya bean, sardine, and dehydrated castor oil, with aqueous alkalies at 225° C. for two to three hours in a stainless steel vessel. The following results, obtained with linseed oil fatty

acids, provide an idea of the extent to which conjugation proceeds. Linseed oil fatty acids (75 g.), caustic soda (75 g.), and water (125 g.), subjected to the above conditions produced a mixture of acids consisting of 41·0 per cent of acids with two conjugated double bonds, and 8·2 per cent of acids with three conjugated double bonds. Tung oil acids, similarly treated, actually revealed a reduction in conjugation but more evidence seems to be necessary on this point.

The presence of conjugated double bonds is very conveniently demonstrated by ultra-violet absorption spectrum measurements.

The conjugation resulting from alkali treatment differs from the conjugation in the acids of the well-known drying oils, dehydrated castor and tung oil, in that it probably occurs in the 10, 12, and 10, 12, 14 positions respectively.[169]

Conjugated oils, it is generally agreed, body more rapidly than the untreated oils. At low viscosities conjugated linseed oil dries faster than ordinary linseed stand oil, but highly bodied conjugated oil loses much of this advantage; also it is reported that none of the conjugated oils so far examined gives harder films than those from the untreated oils.[170] Conjugated fatty acids are said to increase the rate of alkyd formation, but it is not clear whether this is because of an acceleration of the initial esterification reaction or of the subsequent polymerisation.

(*b*) *High Temperature Heat Treatment of Oils like Linseed.*[151]—High temperature treatment (350° C.) at 0·25 mm. with stirring, in an inert atmosphere, has resulted in the conversion of semi-drying oils like grapeseed, tomatoseed or rape oils, into oils with drying properties similar to those of linseed oil.[106]

Bis oil is a product of the high temperature treatment of linseed oil in the presence of air, and although the precise mechanism of the chemical processes involved have not been fully explained, it is known that oils with improved properties are obtained. Bis oils exhibit enhanced drying properties and water resistance, which are equivalent to those of a 20 per cent tung oil-linseed stand oil mixture. Weatherston [181] believes that the oxygen of the air acts as a polymerisation catalyst and is not retained in the molecule. It may be that the improvements in properties resulting from the above treatment are caused by isomerisation of the original oil.

It is claimed also, that irrespective of viscosity, Bis oils are compatible with basic pigments, and that acid values are lower than those of closed pot stand oils of similar viscosity. High temperature oxidation of organic esters, as typified by fatty acid triglycerides, definitely results in a certain amount of decomposition and elimination of fatty acids, and it can only be assumed that in the Bis oil process as used in this country, the acids are distilled away. It is interesting to observe that no claim is made that Bis oils have lower acid values than similar open pot stand oils. These latter are usually of lower acidity than the closed pot variety, and the difference in this case is commonly attributed to loss of acid by

unhampered distillation. The hydroxyl values of Bis oils are lower than those of the ordinary low temperature blown oils, and they do not react readily with certain types of phenolic resin.

Bis oil is made by blowing a selected grade of linseed oil at temperatures about 300° C.[182] A violent exothermic reaction occurs and no further direct heating is found necessary to maintain the temperature.

The Plastybeols are vegetable drying oil products, from linseed oil, produced by an undisclosed method, but different from that used for Bis oils. The method does, however, involve a combination of high temperature polymerisation and oxidation processes, and the improved properties obtained are believed to be explained by induced isomerisation.

Several grades of this type of oil are made as follows : Plastybeol 90 has a viscosity of 90 poises at 25° C., an acid value of about 20, and an hydroxyl value of 30 ; another grade with an acid value of less than 10 is made ; and a third grade with the high viscosity of 150 poises.

The particular advantages claimed for these oils are improved drying speed, film hardness, freedom from tack, and water resistance, by comparison with ordinary stand oils ; but especially a considerably accelerated gelation rate on heating. Plastybeol 90 gels in fifteen minutes at 324° C. and in forty-seven minutes at 315° C. In addition, when used with varnishes based on Congo copal, no maturing is necessary because no subsequent turbidity develops.

A conjugated linseed oil, manufactured in America also by an undisclosed method under the name of Conjulin,[171] is said to gel in about seven minutes at 315° C. Tung oil at the same temperature requires about five minutes' treatment. A temperature of 315° C. is usually regarded in Great Britain as somewhat high for varnish manufacture or oil boiling, except perhaps in the initial stages of oiling down a hot, freshly run copal, and it may be that the close resemblance to the polymerising properties of tung oil by this oil is only exhibited at this rather unusual temperature. It is reasonable to assume that the divergency between Conjulin and similar oils, by comparison with tung oil, will be more pronounced at the more popular varnish-making temperatures. Nevertheless, if makers' claims are widely substantiated in use, production of these oils must be regarded as a meritorious achievement. A conjugated soya bean oil has also been made commercially, but as with Conjulin, details of manufacture are not disclosed.

Cottonseed oil can be converted into a drying oil by simultaneous oxidation and polymerisation treatment.[222]

(c) *Lower Temperature Heat Treatment of Drying Oils in the Presence of Catalysts (e.g. Sulphur Dioxide) under Pressure.*[152]—A rapid drying oil with no tendency to frost is made by heating linseed oil at 196° C., and blowing with sulphur dioxide for one hour, under a pressure of 150 atmospheres. Other oils which have been treated satisfactorily by this process are soya bean, cod and sperm oils.[163]

(*d*) *Treatment of Vegetable Oils by Activated Fuller's Earth.*—This simple treatment was found to give a slight but noticeable improvement in conjugation.[153]

(*e*) *Low Temperature Blowing followed by Solvent Extraction.*—Oils of the type of linseed, hempseed, or soya bean, are blown with air at just above ambient temperature and subjected to solvent extraction with alcohol. A conjugated liquid drying oil, soluble in aliphatic hydrocarbons, is obtained, as the residue.[175]

The Degree of Conjugation of several Varnish Oils.—The following table constructed from the results of Bradley and Richardson (*loc. cit.*), who estimated the proportion of conjugated double bonds in oils by measuring their ultra-violet absorptions at various wave-lengths, shows the distribution of conjugated double bonds in the more popular varnish oils.

Natural Oil	Percentage of Acids with Conjugated Double Bonds.		
	Two Double Bonds.	Three Double Bonds.	Four Double Bonds.
Castor	0·23	0·02	0·0025
Castor dehydrated	28·40	0·19	0·00
Cottonseed	0·41	0·06	0·00
Linseed	0·69	0·12	0·04
Oiticica	0·00	75·80	0·31
Perilla	0·53	0·19	0·06
Sardine	0·66	0·05	0·02
Soya bean	0·79	0·12	0·02
Tung oil	0·00	84·50	0·38

4. *Selective Saponification of Drying Oil Fatty Acids, followed by Esterification.*—In this connection it has been reported that partial hydrolysis of the non-drying cottonseed oil at 100° C. with caustic soda results in the splitting off of the unsaturated fatty acids. The saturated acids are claimed, strangely it seems, to be unattacked. The sodium soaps of the unsaturated acids are treated with mineral acid, the fatty acids liberated, and esterified with glycerol. The resultant oil dries in the amazing time of three hours.[180]

5. *Dimerisation of Drying or Semi-drying Oil Fatty Acids followed by Esterification.*—Oils with inferior drying properties, such as cottonseed, maize, or soya bean oil, by suitable treatment, can be converted into oils, at least the equals of the recognised drying oils. According to Cowan and Falkenburg, the fatty acids from the semi-drying oils are first polymerised to form more complex molecules from two or three acid molecules—dimeric or trimeric acids. After removal of monomeric acid, the polymeric acids are reacted with suitable trihydric or other polyhydric alcohols.[187] Cowan also notes that polymeric acids, whether dimeric or trimeric, from the polymerised oils derived from maize, cottonseed and dehydrated castor oils, were similar in properties. These

polymeric acids are very interesting intermediates, for the dimeric acid has two reactive carboxyl groups and the trimeric acid, three. The polymeric acids may be reacted with polyhydric alcohols to yield polymeric esters with free hydroxyl groups. The free hydroxyl groups may then be reacted with the calculated amount of monomeric fatty acids, which may be the fatty acids of the original natural fatty oil.

Synthetic oils produced by this method dry much better than linseed oil, and have superior alkali and water resistance. These improvements are not, however, observed in an ester gum varnish formulation, but this does not mean that the synthetic oils are generally not particularly satisfactory for varnishes, but rather that they can be exploited to best advantage only with certain other selected varnish constituents. This is, of course, equally true of most raw materials and intermediates.

6. *Esterification of Drying Oil Fatty Acids with Higher Alcohols such as Penta-erythritol, Mannitol, etc.*—A very comprehensive review of the preparation, properties, and uses of polyhydric alcohol esters of fatty acids containing more than eight carbon atoms has appeared recently.[154]

Drying esters from penta-erythritol seem to be a certain step in synthetic drying oil production of the near future. Penta-erythritol will, it is believed, become available at a reasonable price at or before the cessation of hostilities, and much work is already being performed in research laboratories, to exploit its very valuable properties. It is chiefly interesting because of its four reactive primary hydroxyl groups. Some of the penta-erythritol available contains a proportion of dipenta-erythritol, derived from the interaction of two penta-erythritol molecules. The resultant product contains six hydroxyl groups. The presence of dipenta-erythritol, is, therefore, no disadvantage when the object is to build up molecules of considerable size.

The following patent [155] covers the reaction between drying oil fatty acids or the oils themselves and dipenta-erythritol, a reaction occurring with or without the assistance of catalysts. When fatty acids are used, the unreacted acids are removed by extraction with alcohol. The free glycerol, from the reaction with the drying oils is removed by passing a stream of inert gas through the product or by subjecting it to a vacuum distillation. Good water resistance and drying properties are claimed from these esters.

Blagonravova and Drinberg [244] have conducted a considerable amount of work on the esterification of drying oil fatty acids with penta-erythritol, and their final method of procedure was to heat the fatty acids with up to 50 per cent excess of penta-erythritol for six to ten hours at 200°–220° C. Burrell, however, claims a greater reaction rate both for alcoholysis of triglycerides with penta-erythritol, and for esterification of fatty acids, if catalysts in the form of oil soluble salts of lithium, zinc, cadmium and the alkaline earths are present. In particular, the naphthenate, stearate, and resinate, are given as examples of excellent catalysts.[259]

The penta-erythritol-drying oil fatty acid esters show enhanced drying properties as evidenced not only by a greater rate of drying but by harder films. They have, in addition, excellent water resistance.

Blagonravova and Drinberg also demonstrated that the penta-erythritol esters of mono unsaturated fatty acids also possess appreciable drying properties. This seems to open another new field, for the penta-erythritol tetra-oleate air-dried to a dust-free condition in forty-eight hours.

Synthetic oils from drying oil fatty acids and mannitol are also safe prophecies.

7. *Treatment of unsaturated drying oils with halogens or their oxyacids, followed by splitting off of halogen acid, is claimed* to yield oils of enhanced unsaturation.[134]

Unsaturated acids of non-drying oils have been treated also by a similar process to give, ultimately, esters suitable for use in varnishes, for example: oleic acid is chlorinated to give the dichlorstearic acid, and this is reacted with caustic soda to eliminate the chlorine. An acid with two double bonds is set free from the soap, and esterified.[157]

The hypochlorous acid addition compound from octadecadiene 9 : 11 acid triglyceride, described as a chloroxy oil, has been found to have excellent drying properties.[97]

Semi-drying oils and petroleum have been chlorinated and then dechlorinated to provide products with increased unsaturation and improved drying power.[100]

8. *Ozonisation.*—Both castor and grapeseed oil have been subjected to the action of ozone at 150° C., with the elimination of water and an improvement in drying properties.[156] There does not, however, appear to be any indications that this treatment will prove of commercial value.

9. *Treatment of Drying Oils with Maleic Acid.*—A product resembling wood oil is claimed by heating linseed oil at 205° C. for several hours in an oxygen-free atmosphere.[158]

10. *Heat Treatment of Drying Oils with Miscellaneous Reagents at 200° C. or a suitable alternative High Temperature, improves the Rate of Drying.*—The following are reagents credited with this property according to several recent American patents: mineral acids, and acids such as β-naphthol-3, 6, 8-tri-sulphonic and trichloracetic acids; compounds capable of yielding nitrogen-containing acids; naphthylamine; chlorides of zinc and cadmium; sodium hydrogen sulphate and ammonium iodide.[159]

The drying properties of soya bean, corn, and cottonseed oils have been improved by heating at a similar temperature (200°–250° C.) with 0·1 per cent of calcium hydroxide or linoleate, for up to eighteen hours.[176]

11. *Reactions Involving Hydrocarbons and Compounds other than Fatty Acids or their Esters, yielding Oily Products with Drying Properties.*—1 and 2 chloro-1-propene in the presence of aluminium chloride gives a product with drying properties.[160] Olefines may also be polymerised

in the presence of the same reagent to yield drying oils of high molecular weight.[101] Dialkene has been used as the basis of drying oils.[102]

Hydrocarbons, free from oxygen-containing compounds, are reacted with phosgene and aluminium chloride at 40°–80° C. Drying oils, of a fluorescent orange colour, miscible with linseed and other oils, are obtained.[162]

Light oil fractions derived from the pyrolysis of petroleum are polymerised in a solvent with 1·25–1·50 per cent of aluminium chloride. After neutralisation and distillation, an oil drying in about twenty hours is obtained.[172]

Sulphuric acid has also been used as a polymerising agent for unsaturated hydrocarbons from cracked petroleum distillate. After treatment, the acid sludge is removed, and the polymerised hydrocarbons are recovered after neutralisation and distillation. The product hardens on exposure to air.[192]

The esters obtained from a condensation of chlorinated unsaturated petroleum compounds, and the sodium salts of carboxylic acids from the oxidation of petroleum hydrocarbons, possess drying properties.[99]

Hydrogenation and simultaneous polymerisation of vinylacetylene yields drying products.[105]

The Oronite drying oil extenders, formerly known as Orolin, claim to be entirely new aromatic drying oils, and are available in quantity. Their precise method of manufacture is not disclosed, but they are described as unsaturated cyclic hydrocarbon polymers, and are quite distinct from lubricating oil extracts or the by-products from the " Gray " tower process.

Many grades are made, all reddish-brown fluorescent products, varying in consistency from true liquids to soft solids. They are all substantially neutral and have a degree of unsaturation as measured by the iodine value (Wijs) of 160–180^{+}. Their weights per gallon (American) range from 7·9 to 8·6 lb.

They are suggested for use with fatty drying oils but are not recommended as direct substitutes. They may be co-polymerised by heating with the fatty oils, but this is an operation which must be conducted with precaution because the lower members of the series have flash-points as low as 225° F. (C.O.C.), and the most non-volatile product only 480° F. Probably the safest way to use them is as a check back when all lights are extinguished.

Because of their chemical constitution these oils possess good acid and alkali resistance, and excellent solvent properties for most varnish constituents.

The Oronites dry with the usual driers to yield hard tack-free films, although the films are very prone to yellow on ageing.

12. *Introduction of hydroxyl groups into unsaturated oil molecules with poor drying properties*, and the subsequent removal of water by heating in the presence of a catalyst. Soya bean oil is heated with an oxygen-

containing gas under conditions designed to cause hydroxylation without appreciable polymerisation. The product is then "dehydrated" in a manner similar to that employed for castor oil, by further heating with a substance like sodium bisulphate or kaolin. An oil with conjugated double bonds and drying properties, superior to those of the original oil is obtained.[161]

Other oils such as mushroom, tobacco, corn, sunflower and seal oils, have been treated by a similar process involving oxidation by means of air at 150° C., resulting in the introduction of hydroxyl groups, followed by dehydration at 280° C., in the presence of alumina and metallic zinc.[173] In this instance also, the resultant oils are more unsaturated than the original oils and dry better than the ordinary stand oil or oxidised oil. A fraction obtained from the product by acetone extraction resembled linseed oil.

Selenium dioxide, in the proportion of one half molecule to each triglyceride molecule, is capable of oxidising an unsaturated fatty oil, so that an hydroxyl group is induced next to the double bond of one of the acid chains of the oil molecule. After dehydration as indicated above, which results in the production of a conjugated system, a further treatment may be given with the selenium dioxide, to cause more conjugation in the ultimate oil. With linseed oil, nearly complete conjugation is claimed by this method, but it is emphasised that the step by step treatment is necessary if uncontrolled oxidation is to be avoided.[164]

Oleic acid is converted into dihydroxystearic acid from which octadecadiene 8 : 10 acid is obtained by the Kraft reaction,[97] and this is subsequently esterified to provide a drying oil.

13. *Miscellaneous Methods.*—A drying oil has been made from the reaction between rosin and drying oils, or ester gum, at 260°–325° C. using fuller's earth as catalyst.[103] Tall oil has also featured in many so-called synthetic oils of recent years.

The polyesters derived from unsaturated acids like maleic or fumaric acids and glycerol and glycol, set to films at ordinary temperatures, especially if metallic accelerators are present.[104]

Polymerised oils are claimed by pre-treating vegetable or fish oils for periods of from two to ten hours at stand oil-making temperatures (285°–290° C.); the products are then co-polymerised at a much lower temperature (150° C.), with lower diene hydrocarbons, using catalysts such as metallic sodium or diazo-amino-benzene.[174]

Monomeric vinyl compounds have been co-polymerised with stand oil extracts.[188]

The products from both oiticica and po-yok oils, after four hours' treatment at 200° C. with acetic anhydride and anhydrous sodium acetate, can be used with modified phenol formaldehyde resins to give rapid drying water resistant varnishes.[243]

The drying of ordinary drying oils is enhanced, and semi-drying oils are converted into better drying oils, by a prolonged heat treatment

(2–18 hrs.) at 200°–250° C. in the presence of 0·1 per cent of alkaline hydroxide.[212]

Rarer Oils

Bonito Oil

Derived from *Euthynnus pelamys*. This oil is interesting, chiefly because it contains highly unsaturated acids. Ueno and Matsuda[107] have reported the existence of an acid corresponding with $C_{16}H_{30}O_2$, a C_{18} acid with four double bonds, C_{20} acids with four and five double bonds, a C_{22} acid, and an acid with seven double bonds. Subsequent work has shown that the C_{20} acids consist of gadoleic, eicosatetraenic, eicosapentaenic, and docosahexaenic acids. In addition, the presence of a C_{24} acid, named bonitonic acid, is reported, with a formula of $C_{24}H_{34}O_2$.[218] Matsuoka and Ueno[108] have discovered, in addition, the existence of a number of saturated acids; stearic, palmitic, behenic, arachidic and myristic.

Bagillumbang Oil. (Soft Lumbang Oil)

The oil is obtained from *Aleurites trisperma* indigenous to the Philippines. It has good drying properties, due, no doubt, to the high percentage of elaeostearic acid which it contains.[109]

Cacahuananche (Licania arborea) Seed Oil.

This, like oiticica oil, is a product of South America, and the oil resembles Brazilian oiticica oil, not only in its source of origin, but in its composition also. It is, in fact, actually described as Mexican oiticica oil.

The percentage composition of its glycerides is :

	Per cent[226]
Licanic	73·3
Linoleic	7·6
Oleic	5·4
Elaeostearic	1·6
Saturated	11·6
Unsaponifiable	0·5

but the composition varies according to the ripeness of the fruit.

It polymerises very well, giving a Browne heat test figure of 15·5 mins.

There is every indication that it is a valuable drying oil for use in varnishes, and it can be handled and used in a manner similar to that for oiticica oil.

Oil from Nuts of the Cansancao Tree

This tree, indigenous to Brazil, yields nuts, the kernels of which provide about 30 per cent of an oil which resembles refined cottonseed oil. It has an iodine value of 130 and is suggested as a substitute for soya bean oil. The tree is known also as Peñas, *Cnidoscolus marcgravii*, and *Jatropha oligandra*.[239]

Chia Oil

This is derived from the Mexican *Salvia hispanica*. Experimental plantings in the U.S.A. have proved to be unsuccessful. The percentage compositson of the oil is

	Per cent
Linoleic acid	45·2–30·3
Linolenic acid	39·3–50·2
Oleic acid	0·7–0·0
Saturated acids	8·1

The heat treated oil dries better than linseed, but not quite so good as perilla oil. It does not polymerise so rapidly as linseed oil on heating, and yellows more on stoving. Gardner [110] has suggested it as a substitute for linseed oil in varnishes.

Corn Salad Oil

This oil resembles poppyseed oil in composition. It dries in about forty-eight hours without drier.[111]

Eel Oil

This oil is obtained from *Anguilla fluviatilis* and has fatty acids of the following composition :

	Per cent
Linoleic acid	31·5
Linolenic acid	17·0
Oleic acid	33·2
Saturated acid	13·5

Pritzker and Jungkung obtained an iodine value of 133 for the extracted oil.[247]

Elderberry Seed Oil

It is derived from the seeds of *Sambucus canadensis*. Although its iodine value, 162–171·7, is lower than that of linseed oil it is claimed to dry quicker and for this reason it is a possible substitute.[112]

Oil from Garcia Nutans

Gardner and Westgate have examined a sample of oil from Mexican seed with encouraging results. The tree, which is of the Euphorbiaceae class, is really native to Venezuela, but it occurs also to some extent in Mexico. The Mexican oil was found to have similar polymerising properties to tung oil, with superior alkali resistance.[245]

Grapeseed Oil

The oil is obtained by expression from the seeds of *Vitis vinifera* and *Vitis riparia*, which are found in France, Italy, Germany and the United States of America. The composition of its acids is

	Per cent
Saturated acids	5·3– 9·2
Oleic acid	32·1–44·3
Linoleic acid	46·0–55·3
Linolenic acid	0·1– 2·3

Varnish Constituents

In Italy the dry seeds of both black and white grapes are processed and the former gives a slightly better yield. The oil is obtained by expression, or extraction with solvents such as benzine, ether or trichlorethylene.[113] Extraction of the ground seed gives better yields than pressing.

Its value as a paint or varnish oil has been estimated differently by various workers, but generally it may be claimed to have fair drying properties. Thus, its inclusion in varnishes becomes a possibility. It is said to dry quickly but to retain its tack for a long time. Gardner states it to be superior in its properties to soya bean oil, whereas Brambilla and Balbi claim it as a satisfactory substitute for linseed oil or for use in admixtures with it.[114] Balbi subsequently classified it among sunflower, soya, poppyseed, and tobacco seed oils, and pointed out that for two years it had been used successfully in the Italian Paint and Varnish Industry. An opposing view is held by others, who prophesy few applications for it by reason of its poor drying properties, but a large volume of work has been conducted on it in Italy during the war, and although absence of other drying oils may have stimulated this interest, its properties must be worthy, in some measure, of exploitation. As a mixed stand oil, consisting of one part grapeseed oil to two parts of tung oil, it may become useful.[115] Pale grapeseed oil stand oils with high acid values are prepared by heating at 330° C. for eight hours in an atmosphere of carbon dioxide. The stand oils are said to have good drying properties.[116] For the preparation of stand oils it is necessary to use the refined oil and the actual heating is best conducted under reduced pressure.[242]

Hempseed Oil

Hempseed oil has attained some popularity as a paint oil in Continental Europe. It is produced from the seeds of *Cannabis sativa* which grows chiefly in North America, Japan, India and Western Europe, although some have been cultivated in the United States of America. The percentage composition of its acids is

	Per cent
Saturated acids	10·1
Oleic acid	12·6
Linoleic acid	53·0
Linolenic acid	24·3

The oil possesses a characteristic green colour, and although it does not dry so quickly as linseed oil, it is claimed to have better non-yellowing properties and water resistance.[117] Heat-treated oils exhibit improved drying properties.

Isano Oil

The oil is obtained from the kernels of the nuts of an African tree, *Ongokea klaineane*. The oil in the untreated condition does not dry,

but heat treatment induces striking drying properties. Heating causes quite a violent exothermic reaction, and as with tung oil, careful supervision is needed to avoid gelation. One method of treatment consists in refluxing the isano oil with a high boiling petroleum hydrocarbon, and removing the solvent subsequently by distillation. It is best heat treated in the presence of other varnish making oils, and the resultant products are claimed to have exceptional properties. Even when isano oil is diluted with four times its own weight of linseed oil, the mixture polymerises rapidly in three hours at 250° C. to give a fairly viscous stand oil. The resultant oil dries very much more rapidly than linseed stand oil, and has much superior water resistance. Similar advantages are claimed for soya bean-isano stand oils.[253]

Pierre has published some information on the composition of the oil, and in addition to saturated acids and acids like oleic, it contains "erythrogenic acid" which he believes has a double bond and two triple bonds ($C_{18}H_{26}O_2$).[254] Steger and Van Loon report the presence of at least one unsaturated hydroxy acid.

Hisperis Matronalis Seed Oil

Steger and Van Loon have noted its resemblance to linseed and perilla oils. If it is anything like the latter, it should be a useful varnish oil. Its iodine value is given as 190–198, and varnish makers will be interested to examine it further if it promises to be regularly available in quantity.[240]

Lallemantia Oil

Oils from various species of Lallemantia, native to Russia and Spain, have been examined with encouraging results. The oils possess good drying properties and are possible substitutes for linseed oil.[209]

Lumbang Oil. (Candlenut oil)

The oil is obtained from the seeds of *Aleurites moluccana* which is found in the Philippines, India, Australia and Java. Cultivation has been tried also in Florida, Brazil and the West Indies. The percentage composition of its acids is

	Per cent
Saturated acids	2·1– 2·8
Oleic acid	41·1–56·1
Linoleic acid	34·4–49·0
Linolenic acid	6·7– 7·8

It has been used in paints and varnishes but its drying properties are not too good. Gardner showed that on heating a sample of oil with acid value 46, it decreased to 16·5.[118]

Nigerseed Oil

It is the oil from the seeds of *Guizotia oleifera* or *Guizotia abyssinica*, which are grown in Abyssinia, the Indies and India. The oil has a

pleasant smell and a golden-yellow colour. The approximate percentage composition of its acids is

	Per cent
Saturated acids	9·8
Oleic acid	32·9
Linoleic acid	57·3

Vidyarthi and Mallya have recorded the actual percentage composition of the oil on the individual mixed triglycerides present, which were separated and named.[221]

The undriered oil dries in four to eight days but the addition of driers reduces this to one day. Heat treatment of the oil reduces the drying time to eleven hours with driers.[119]

Orange Seed Oil

The percentage composition of the fatty acids of this oil indicates its possibilities in varnish manufacture. A recent analysis gives the following :—

	Per cent
Linoleic acid	46·7
Linolenic acid	0·6
Oleic acid	21·0 [228]

Poppyseed Oil

Papaver Somniferum grown in India, Asia Minor, Russia and France is the source of this oil. It is generally obtained by cold or hot expression. The percentage composition of its acids is

	Per cent
Saturated acids	7·7
Oleic acid	30·1
Linoleic acid	62·2

Sun-bleached oil for artists' use has been known for centuries but it enjoys no popularity as a constituent of decorative varnishes.

There is another oil, known as Mexican poppyseed oil (*Argemone mexicana*), but a sample of this from a Nigerian source is reported to possess poor drying properties.[148]

Po-Yok Oil

It is sometimes described also as po-yoak oil. The former is apparently derived from the seeds of *Afrolicania elaeosperma*, and po-yoak oil from *Parinarium sherbroense*. Both species are indigenous to West Africa and it is possible that the oils available commercially are mixtures of the two types.

The oil from *Parinarium sherbroense* has been examined by Steger and Van Loon [120] and found to contain approximately three parts of licanic acid to two parts of elaeostearic acid, some stearic and oleic acids. They conclude it to be between tung and oiticica oil in its properties, although Rheineck [121] observes that it approximates more closely to oiticica oil. In his opinion, since the source of the oil is at present confined to Sierra

Leone, it could not supply the demands of industry for another twenty years.

The possibilities of po-yok oil as a substitute for tung oil in varnishes have also been examined critically by the Research Association of British Paint, Colour, and Varnish Manufacturers, and their conclusions have been published in Research Memorandum No. 53, 1942. The following notes summarise the investigation.

The oil resembles tung oil in that it webs on drying. The undriered oil becomes skin dry in twenty-four hours, but several days are necessary for through-drying. The resultant film is cloudy and inelastic. With cobalt driers through drying is effected in twenty-four hours. In varnishes, those based on po-yok oil require 10–25 per cent. longer drying time than similar tung oil varnishes.

The bodying rate of po-yok oil on heating is between that of tung and linseed oils, but much nearer the former. It yields a light stand oil after thirty minutes treatment at 220°–240° C. The bodied oil appears to dry appreciably more quickly than the raw oil.

The oil is compatible with the normal natural and synthetic resins. Films of suitably formulated varnishes, involving modified phenolic resins, resist the action of boiling water in a manner similar to corresponding tung oil films. The po-yok films also demonstrate good cold water and alkali resistance.

Ragweed Seed Oil

This is another of the rarer oils which might be valuable as a varnish oil. It dries fairly well and polymerises on heating. The percentage composition of its fatty acids is given as :

	Per cent
Linoleic acid	70·0 [220]
Oleic acid	20·0
Saturated acid	10·0

Road Thistle Seed Oil (Onopordon Acanthium Seed Oil)

This oil was brought to light by Steger and Van Loon, who comment upon its similarity to poppyseed oil. The percentage composition of its acids is given as :

	Per cent
Linoleic acid	64·0 [240]
Linolenic acid	3·6
Oleic acid	*25·5*

Safflower Oil

Carthamus tinctorius, which grows in Egypt, Russia and India, is the source of this oil. The percentage composition of its acids is

	Per cent
Saturated acids	10·0– 6·2
Oleic acid	26·3–38·0
Linoleic acid	51·0–67·4
Linolenic acid	0·1– 1·0

On heating, the oil deposits no break. Rehbein states that the oil dries as quickly as linseed oil; others say that it resembles soya bean oil, but Van Loon agrees that it can replace linseed oil for some purposes.[122] The processes involved in the drying of this oil on exposure to air or oxygen are rather unusual. The weight of the drying film increases initially by about 9 per cent. because of oxygen absorption, but thereafter a rapid decrease in weight occurs. After fourteen days, the film loses not only its initial gain in weight but a further 5 per cent also.[201]

It bodies more slowly than linseed oil and when blown exhibits improved drying properties. This improvement is perceptible after blowing with air at 50° C. for forty hours, or with ozonised air for fifteen to twenty hours. A boiled oil with cobalt as drier, prepared by Remington, dried in eighteen hours. The relative durabilities of safflower oil and linseed oil are controversial.[123] It is valuable, however, by reason of its non-yellowing properties which have been recognised and are being exploited. The fact that the gel it forms on prolonged heating is easily dispersed in solvents has prompted the suggestion that it might be used in wet-on-wet paints.[124]

Sandal Seed Oil

This has been examined by Sreenivasaya and Narayana[125] who report that the oil dries well to give glossy and elastic films, which have good insulating properties.

Stillingia Oil

The oil is obtained from *Stillingia sebifera* or *Sapium sebiferum* which grows in China, India, Florida, Texas and California. The percentage composition of the fatty acids as glycerides is[124]

	Per cent
Saturated acids	9·1– 6·4
Oleic acid	26·4–25·5
Linoleic acid	51·9–58·5
Linolenic acid	10·9– 8·0

The oil is satisfactory for use in varnishes and is intermediate in properties between linseed oil and tung oil. It polymerises readily at 280° C. to form stand oils.[126]

Stinging Nettle Seed Oil

German sources record the possibilities of the use of this oil, obtained from seeds by petroleum ether extraction. The iodine value of 151·2 certainly makes the oil interesting, and its drying properties are between those of hemp and poppyseed oils.[237]

Sunflower Oil

It is derived from *Helianthus annus* which grows prolifically in Russia, Argentine, India, China, Hungary, Roumania, Yugoslavia, the United States of America and Uruquay. It is usually obtained by expression. The percentage composition of its acids is

	Per cent
Saturated acids	6·0– 9·6
Oleic acid	34·1–42·0
Linoleic acid	52·0–58·5

Even with cobalt drier, sunflower oil requires twenty-six hours in which to dry but the removal of elaidin promotes a marked improvement in drying properties.[127] Additions of 30–40 per cent. of sunflower oil to linseed oil yield a mixed oil of good drying properties.[128]

Sunflower oil is used generally after blowing or as a boiled oil. Boiled oil, drying in about twenty-seven hours, is prepared using lead and manganese driers.[129] Like safflower oil its chief use is in non-yellowing media.

Tobacco Seed Oil

Tobacco (*Nicotiana tobacum*) seed oil is produced in quantity in India (Madras Presidency) and could be, if desired, in Roumania also.

The composition of this oil given by Roberts and Schutti indicates its possibilities as a drying oil.[130]

	Per cent
Saturated acids	7·9
Linoleic acid	70·4
Oleic acid	16·2

This composition is not, however, agreed unaninously, for Indian workers on the product from Virginia tobacco, grown in Madras, report the following analysis :—

	Per cent
Myristic acid	1·8
Palmitic acid	7·8
Stearic acid	5·6
Oleic acid	30·2
Linolenic acid	54·6

The oil upon which these figures were obtained had an unusually low iodine value of 112·2 as against about 140. This was attributed to climatic conditions and may partly explain the difference in composition.[227] The possibility of such wide differences is a factor which a user cannot ignore.

With driers the oil dries slightly better than linseed oil, and, moreover, it has reasonable exterior durability. Stand oils can be prepared from it in the usual way by heating at 290°–300° C., and about eight hours' treatment at 290° C. is necessary to give an oil of medium viscosity. The natural oil is dark in colour and the resultant stand oils are even darker, but if the original oil is carefully refined satisfactory pale products are obtained.

Tomato Seed Oil

Some attention has been devoted to a study of this oil in respect to its suitability as a paint and varnish oil. Ovanesian has reported on a sample of oil with an iodine value of 114.

Varnish Constituents

The untreated oil required sixteen to seventeen days to dry but a boiled oil dried in two days.[131] The dried film tends to remain tacky but the polymerised oil has good drying properties and may be used in varnishes as a substitute for linseed oil, or in admixture with it.[132]

Oil from Vernonia Anthelmintica Seeds

This oil is interesting because it resembles castor oil, in that about 60 per cent of the total weight of the fatty acids obtained from it consist of an isomeric ricinoleic acid—a straight chain hydroxy acid, $C_{18}H_{34}O_3$, which is *l* rotatory. Halogen substitution occurs readily at the hydroxyl group.[210]

Walnut Oil

The oil is expressed from the kernels of *Juglano regia*. The approximate percentage composition of its fatty acids is

	Per cent
Saturated acids	7·6– 9·4
Oleic acids	17·6–28·9
Linoleic acid	47·6–62·7
Linolenic acid	10·0–15·9

It is used chiefly as an artists' oil, and exhibits little tendency to yellow. A sample of Iguape Walnut oil examined by Silva[133] gave an iodine value of 160·2, which is outside the normal limits of 140–150. The untreated oil dried slowly, but a light stand oil made by heating at 280° C. for four hours dried satisfactorily, and could substitute linseed oil.

Wild Rose Seed Oil

The oil from wild-rose hips, constituting about 9·4 per cent of the total weight, has been examined for drying properties. The percentage composition of the fatty acids is

	Per cent
Linoleic acid	56·71
Linolenic acid	9·45
Oleic acid	29·32
Solid acids	4·50

After heat treatment at 250° C. the oil dries to a tack-free condition, but the untreated oil shows poor drying properties and a tendency to "crawl."[220]

Substitution of Tung Oil

The question of the substitution of tung oil by some other oil has been tackled by every varnish maker at some time or another. Before analysing the claims of the many substitutes which have been advocated, it is well to enumerate the important properties of tung oil. It is used primarily to provide varnishes which dry rapidly with freedom from residual tack. With careful formulation it yields, with modified and unmodified phenol formaldehyde resins, varnishes of outstanding durability, water and chemical resistance.

It is obvious that every case of substitution must be considered on its merits, since oil length and ratio of oil constituents are important controlling factors.

Apart from tung oil from sources other than China, there is only one oil which can replace tung oil satisfactorily where it is unnecessary to consider these factors. Direct substitution is possible with Trienol $[CH_3(CH_2)_3\ CH{=}CH{-}CH{=}CH{-}CH{=}CH(CH_2)_7(COO)]_3\ C_3H_7$, which is the triglyceride of an acid containing three conjugated double bonds as in tung oil. It has been claimed that Trienol is prepared by dehydrating castor oil, treating the dehydrated oil with hypochlorous acid, and eliminating hydrochloric acid and water from the additive compound thus formed.[134] This mechanism of the reaction as outlined by Blom has been criticised and shown to be untenable. The only differences between Trienol and tung oil are that the gel obtained by heat treatment of the former is sticky rather than crumbly, and the acid value of Trienol is higher than that of tung oil. Neither of the differences, however, are of fundamental importance. The introduction of Trienol has not, as yet, eased the tung oil position, for, as indicated already, it has not become available in substantial quantity.

The natural oil which resembles tung oil most in its properties is Po-Yok oil, but, as stated by Rheineck (*loc. cit.*), the possibility of it playing the rôle of tung oil completely is very remote, in view of the inadequacy of supply. An interesting report by Westgate states that the oil from *Garcia nutans* compares very favourably with tung oil.[200]

The remaining oils can substitute tung oil only in special cases. Oiticica oil possesses the characteristic odour of tung oil. Unlike tung oil, unless special care is taken at its expression to ensure permanent fluidity, it will be more difficult to handle subsequently in its pasty form, and will deteriorate seriously on storage as already described. Varnishes made from it will be darker than the corresponding tung oil varnishes although the dried films will exhibit no difference in colour. In medium and long oil varnishes generally, the substitution of oiticica oil will result in definitely slower drying, and a lower resistance to water and chemicals. A compromise can be effected, however, by using blends of oiticica oil and tung oil. For short oil varnishes, gold-sizes, and short oil stoving media, oiticica oil can replace tung oil without any detrimental effect. For exterior varnishes where durability is important substitutions should be made with caution. For the cheaper type of boat varnish on an ester gum basis oiticica oil is inferior to tung oil for durability. Oiticica oil tends to become brittle on ageing and its combination with ester gum provides the ideal condition for this to become apparent. The embrittlement can be checked by the inclusion of linseed or similar oils but this will cause a further delay in the drying. The inferior durability of oiticica oil is demonstrated also in modified phenol formaldehyde varnishes. With pure oil-reactive phenol formaldehyde resins oiticica oil yields products of excellent durability, which have been claimed by some

to be superior to similar tung oil varnishes.[135] Oiticica oil reacts more rapidly with pure alkyl phenolic resins than tung oil. In varnishes containing large amounts of linseed oil in relation to tung oil, oiticica oil can be used without serious loss of essential properties.

Another aspirant to the position of tung oil is dehydrated castor oil. In spite of the many exaggerated claims it is, by no means, a direct substitute. Its inferiority is particularly evident in its slowness of dry. Whilst it sets quickly it retains a strong surface tack which lingers for many hours. In quick-drying exterior varnishes used in processes which necessitate rubbing down and the application of successive coats, this residual tack is a distinct disadvantage. Similarly, in stoving varnishes and enamels where absence of residual tack is important, dehydrated castor oil will be found rarely suitable. The foregoing is not recorded of dehydrated castor oil disparagingly, for it possesses certain valuable and unique properties, but to emphasise its dissimilarity to tung oil. Unlike oiticica oil it does not become brittle on ageing and has a durability superior to that of tung oil. In short oil varnishes or in exterior varnishes where linseed oil preponderates it can replace tung oil.

Perilla oil is not a direct substitute for tung oil in any circumstances. It dries much more slowly and has inferior water and chemical resistance. In exterior varnishes, however, rich in linseed oil and containing a small proportion of tung oil, it can replace a mixture of three parts of linseed oil and one part of tung oil with advantage. A varnish thus reformulated would exhibit little difference in speed of dry but a permanently improved gloss and enhanced durability.

Complete reformulation of a varnish will sometimes provide the means of partly eliminating tung oil; for example, the varnish may be shortened or resins such as ester gum, limed rosin, copals or copal esters replaced by harder modified phenol formaldehyde resins. Varnishes containing small quantities of tung oil may have this substituted in some circumstances by blown linseed oil, if resistance to water is not an essential consideration.[136]

Oil-chlorinated rubber and oil-cellulose ether compositions have been suggested as tung oil substitutes but little progress has been made with them.

Drinberg[137] claims that the pentaerythritol ester of linseed fatty acids, or highly unsaturated fatty acids of Japanese sardine oil, can substitute tung oil.

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CONSTANTS OF OILS

Oil.	S.G.	R.I.	A.V.	S.V.	I.V.	Reference.
Almond	0·918 (15·5° C.)	—	0·5–5·0	192·0	99·0	1
Amoora	0·939 (15° C.)	—	—	189·7	134·9	2
Apricot kernel	0·9191 (15° C.)[3]	—	—	188·0[5]	96·0[5]	2
	0·9204 (15° C.)	—	—	198·2	103·7	2
Arachis (groundnut, peanut)	0·9175 (15·5° C.)	—	10·0	193·0	90	1
Argemone	0·9247 (15·5° C.)	—	—	137·8	119·9	6
	0·9259 (15·5° C.)			190·3	122·5	6
Basswood	0·938 (15·5° C.)	—	—	178·1	111·0	7
Beechnut	0·9205 (15° C.)[8]	—	—	196·3[10]	111·2[11]	—
	0·9225 (15° C.)[9]	—	—	191·1[11]	120·1	—
Ben	0·9120 (15° C.)[12]	—	—	184·6	72·2	2
	0·9199 (15·5° C.)[2]	—	—	187·7	112·6	2
BONITO	0·9295 (15° C.)	1·4878 (20° C.)	25·6	182·1	209·7	13
Brazil nut	0·9180 (15° C.)	—	—	193·4	90·6[14]	
					106·22	11
Buffalo gourd seed oil	—	—	—	—	140·8	—
CACAHUANANCHE seed oil (*licania arborea*)	—	1·5163	0·8	187·3	153·0	86
	0·9707 (22° C.)[88]	—	2–11·2[88]	165·4[85]	—	—
Cameline { German	0·9200 (15° C.)[15]	—	—	188·0	135·3	11
Cameline { Sesamé	0·9260 (15° C.)	—	—	—	142·4[16]	11
CANDLENUT (LUMBANG) (*aleurites moluccana*)	0·925 (15·5° C.)	—	—	193·0	164	2
Castanha de cotia (Oil from)	—	—	0·7	194·2	153·5	83
CASTOR	0·964 (15·5° C.)	—	—	180·0	88	1
CASTOR DEHYDRATED (DIENOL)	0·935	1·4835	4·3	190·5	134	17*
Cedar nut	0·932 (0° C.)[18]	—	—	191·8[18, 19]	150·0[18]	—
	0·930 (15° C.)[19]	—	—	—	159·2[19]	—
Cherry kernel	0·9235–0·9238	—	—	194·9	110·8	11
	0·9285 [20]	—	—	193·4[20]	114·3[20]	11
CHIA	0·9338 (15° C.)	1·4855	0·6	192·2	196·3	—
Corn salad	—	—	1·2–3·7	—	145	21
COTTONSEED	0·923 (15·5° C.)	—	< 0·5	193·0	110·0	1
Croton	0·9375 (15·5° C.)	—	—	192·9[23]	88·9	2
				215·0	89·1	2
Clover (white)	—	—	—	189·5	119·7	2
Clover (red)	—	—	—	189·9	124·3	2
Coconut	0·9258 (15·5° C.)	—	10	257·0	8·5	1
Cod liver	0·925 (15·5° C.)	—	Variable	185·0	140·0	1
					170·0	1
Cramp fish	0·909	—	0·8	—	107·3	2
Dolphin body (Black-fish)	0·9266 (15° C.)	1·4708[26]	—	197·3[24]	32·8–	—
				290·0[24]	99·5[24]	
					126·9[25]	—
ELDERBERRY SEED	—	—	—	—	162·0[27]	—
					171·7	—
Essang (nsasana or sanga-sanga)	—	1·5054	—	193·1	192·0[28]	—
Fennel	0·9248 (15° C.)	—	—	196·4	116·2	—

* The constants of this oil will vary considerably, according to the degree of polymerisation and the method of manufacture.

CONSTANTS OF OILS—*Continued*

Oil.	S.G.	R.I.	A.V.	S.V.	I.V.	Reference.
Fenugreek seed oil (*trigonella foenum graecum*) . .	—	1·5789	—	—	158·4	85
Firseed . .	0·9215 (15° C.)[28]	—	—	191·3	118·9	11
	0·9312 (15° C.)	—	—	—	120·0	11
Oil from Garcia Nutans . .	—	1·525	—	189·2	177·9	90
Grapeseed . .	0·9225 (20° C.)	1·4765	4·7	184·4	123·7	30
Garden rocket .	0·9282[9]	—	—	191·8	154·9	11
					155·3	11
Haddock liver .	0·9335	—	—	188·8	154·2	2
	0·9298 (15° C.)	—	—	—	—	—
Hamemalis . .	0·918 (15° C.)	—	—	—	69.0	—
Henbane seed .	0·939 (15° C.)	—	—	170·8	138·0	31
Herring . .	0·9202 (15° C.)	—	—	179·0	131·0	25
	0·927 (15·5° C.)[12]	—	—	193·7	142·0	25
Hempseed . .	0·9391	—	—	191·0	148·0	2
Hipberry seed .	—	—	—	—	155·2	32
Juglans manschurica (Oil from) .	—	1·4790	—	—	158·0	33
Kapok . . .	0·9237 (15° C.)[34]	—	—	181·0[35]	117·9[35]	—
				205·0[36]	129·0	—
Lallemantia . .	0·9336 (20° C.)	—	—	185·0	162·1	37
Lallemantia (Russian and Spanish)	0·9335 (15° C.)	1·484	—	189·8	177·5	209
	0·9399 (15° C.)	1·485	—	195·3	197·0	—
Ling liver . .	0·9200 (15° C.)	—	10·9	184·1	132·6	25
Luffa seed . .	0·9254 (15·5° C.)	—	—	187·8	108·5	2
LINSEED . .	0·933 (15·5° C.)	1·4831	0·0–12·0	190·0	170·0	—
					190·0	—
Linseed (American and Canadian) .	—	—	—	—	127·8	
					202·8	91
Maize . . .	0·925 (15·5° C.)	—	6·0	191·5	119·2	1
MENHADEN . .	0·931 (15·5° C.)	—	7·0	193·0	160·0	1
Monkey face tree kernel (oil from *Mallotus philippinensis*) . .	0·9333	1·5156	11·3	207·6	157·3	89
Mulberryseed oil .	0·931	—	—	196·4	140·1 (fatty acids)	87
Nicotiana rustica (Oil from) .	—	—	28·0	—	152·0	38
Niger . . .	0·9270 (15·5° C.)[39]	1·472	—	188·9[5]	126·6[5]	—
	0·9248 (15° C.)[5]	—	—	192·2	133·8	—
OITICICA . .	0·9770 (20° C.)	1·5090	< 6·0	186·0	140·0	40
	0·9880 (20° C.)	1·5130	—	193·0	150·0	40
Olive . . .	0·916 (15·5° C.)	—	0·5–50·0	190·5	83·0	1
Onguekoa (Oil from)	—	1·5098	—	—	232·0	41
PERILLA . .	0·937 (15·5° C.)	1·487	—	193·4	193·3	42
Ocymoides—						
black . .	0·9350 (15° C.)	1·475	1·2	192·6	—	43
white . .	0·9344 (15° C.)	1·475	2·3	196·8	—	43
Burma . .	0·9336 (15·5° C.)	1·4816	1·7	191·3	193·4	44
Nankinensis .	0·9348 (15° C.)	1·474	2·6	189·0	—	43
				193·0	—	43

CONSTANTS OF OILS—*Continued*

Oil.	S.G.	R.I.	A.V.	S.V.	I.V.
Po-YOK	0·9612 (15° C.)	1·5082	6·0	188·0	149·9
Psoralea drupacea (Oil from)	—	—	—	130·6	164·9
Poppy	0·925 (15·5° C.)	—	1·5	192·5	134·0
Palm	0·922 (15·5° C.)	—	20–185	201·0	54·0
Porpoise body	0·926 (15·5° C.)[30]	—	—	218·8[35]	119·4[25]
	0·937 (16° C.)[47]	—	—	195·0	—
Pumpkin seed	0·9197 (15·5° C.)[48]	—	—	188·4[10]	113·4[50]
	0·925 (15° C.)[40]	—	—	190·2	130·7[49]
Rape (colza)	0·9155 (15·5° C.)	—	<4·0	175	100·0
Ravison (Black sea rape)	0·9175 (15° C.)[51]	—	—	174[53]	101·4[16]
	0·9217 (15·5° C.)[52]	—	—	179·3[52]	121·7[52]
Rubber seed (para)	0·9302 (15° C.)	—	—	206·1	128·3
Seal	0·9240 (15·5° C.)[30]	—	—	178·0[56]	127·0[56]
	0·9263 (15° C.)[55]	—	—	196·2[55]	152·4[57]
Shark liver	0·9105 (15° C.)	—	0·9–6·2	146·1	111·9
	0·9177 (15° C.)	—	—	163·5	136·0
Strawberry seed	0·9345 (15° C.)	—	—	193·7	180·3
,, (Swiss)	—	—	—	—	157·7–165
SUNFLOWER	0·9240 (15° C.)[30]	—	—	188·0[11]	119·7[11]
	0·9360 (15° C.)[59]		—	194·0[60]	135·0[61]
Sesamé (Gingelly)	0·923 (15·5° C.)	—	5·0	192·0	105·0
SARDINE (Japanese)	0·932 (15·5° C.)	—	—	195·0	181·0
	0·934 (15·5° C.)	—	—	196·0	187·0
,, (Californian)	0·923	—	0·5–1·0	180·0	190·0
				190·0	195·0
STILLINGIA (Chinese)	0·938 (15° C.)	1·4817	3·7	206·2	169·0
	0·935 (15° C.)	—	—	—	—
,, (American)	—	1·4830	3·1	211·7	176·1
SAFFLOWER	0·9251 (15·5° C.)	1·477[65]	—	186·6	129·8
	0·9280 (15·5° C.)	—	—	193·3	149·9
Sandal seed	0·925 (25° C.)	1·476	9·0–15·0	185·0	170–17[illegible]
	0·950 (25° C.)	1·480	—	195·0	130–13[illegible]
SOYA BEAN	0·925 (15·5° C.)	—	0·3–5·0	192·0	130·0
Tobacco seed oil	0·926	—	—	—	140·3
Tunny (Sardinian)	—	—	—	—	149·7
TUNG (Chinese)	0·939 (15·5° C.)	1·518	<5·0	189·0	155·0
	0·943 (15.5° C.)	1·522	—	195·0	167·0
,, (Japanese)	0·9313 (25° C.)	1·5059	0·6	190·0	145·2
,, (Kenya)	0·0361 (25° C.)	1·5181	0·4–0·6	192·6	167·7
	0·9358 (25° C.)	—	—	194·4	168·0
,, (Java)	0·9421 (15° C.)	1·5200	0·2–6·7	194·7	166·9
	0·9360 (15° C.)	1·4860	—	190·2	160·3
,, (India)	0·9391 (15·5° C.)	1·514	0·2–0·3	192·3	175·5
,, (Argentine)	0·9334((25° C.)	1·5178	0·4	—	167·0
Tomato seed	—	—	2·8	—	114·0
TRIENOL (Synthetic Tung oil)	0·928	1·5175	8·2	190·0	244·5
Tea seed	0·911 (20° C.)[75]	—	—	188·3[75]	88·0[78]
	0·927 (15° C.)[76]	—	—	195·5[77]	90·4[79]
Walnut (Iguape)	—	—	2·8	—	160·2
Walnut	0·926 (15·5° C.)	—	—	193·0	140·0
				196·0	150·0
Whale	0·922 (15·5° C.)	—	—	188·0	115·0
Wheat	0·9245 (15° C.)	1·4832 [81]	—	182·8	115·0
	0·9374 (15° C.)[81]	—	—	190·3[81]	—
Wild rose seed	—	1·4792	—	—	154·9

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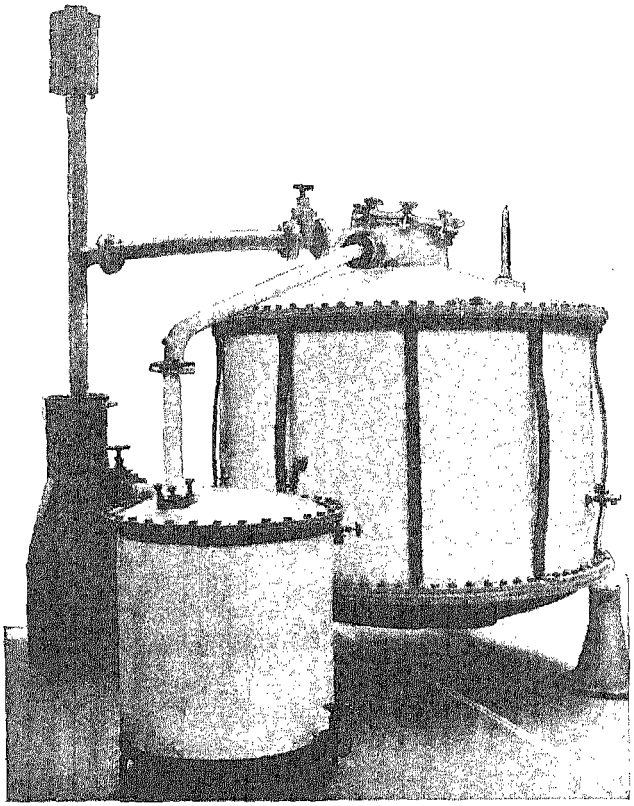
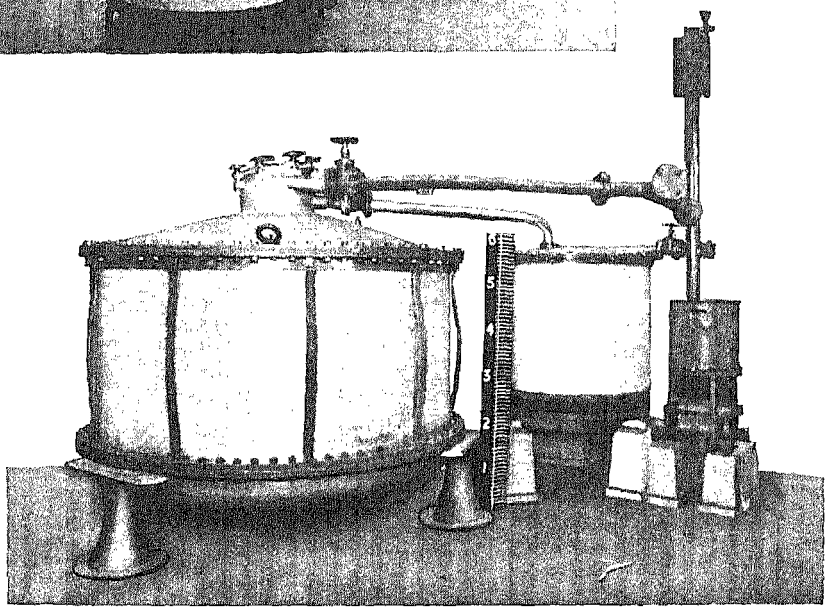


"Sommier" Stand Oil Plants; 3 Ton, and below 5 Ton.



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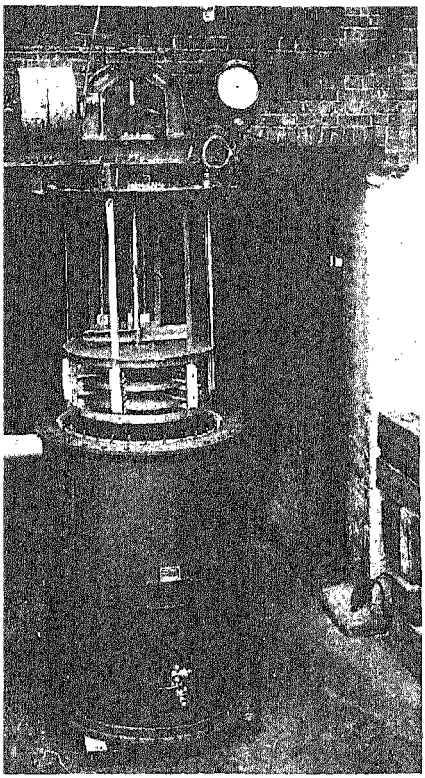
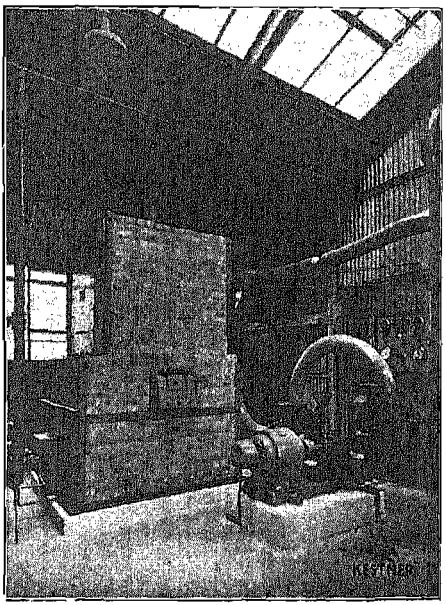


Isolectric Heating Plant.

Gas-Fired Absorber (Merilene System).



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CHAPTER 2

ACIDS

ORGANIC acids, both aliphatic and aromatic, form a useful class of raw materials for varnish manufacture.

Fatty Acids

These are undoubtedly the most important of all the acids. They are obtained from oils or fats by hydrolysis either by steam, acid or alkali treatment or by the action of enzymes. They may be either solid, pasty or liquid, but if in either of the latter two conditions, they should be stored only in well-coopered wooden barrels. Contact with iron or air causes discoloration and this is a defect to be avoided. Fatty acids in the liquid state have a strong tendency to seep out of their containers and care should be taken to ensure that the containers are adequately sealed. Fatty acids vary in colour from almost colourless to yellow, and this depends upon the method of manufacture and the degree of contamination and oxidation. Bulk storage is inadvisable for the varnish maker in view of deterioration, and acids should be used as required from barrels. All linseed fatty acids should give clear solutions with carbon tetrachloride. Cloudy solutions indicate the presence of moisture or metallic compounds which may have been used as catalysts. Zinc compounds have led to insoluble products in the manufacture of alkyds and have revealed themselves as serious bittiness which only filtration removes.

Brambilla has conducted research on the high temperature decomposition of linoleic acid This is interesting, for linoleic acid is a constituent of linseed and other vegetable oil fatty acids, and there are occasions when these acids are involved in high temperature varnish making processes. Linoleic acid, heated to 325° C. in an atmosphere of nitrogen, yields, in addition to water, carbon dioxide, and a carbonaceous residue rich in hydrocarbons, propionic, butyric, hexoic, glutaric and sebacic acids.[1]

The most important use of fatty acids is in the manufacture of alkyd resins, and the commoner acids are those from linseed, soya, dehydrated castor, tung, olive, cottonseed, and palm oils. Stearic acid is also important. The first four acids are used in air drying or stoving alkyds, while the remainder are used in non-drying, non-discolouring alkyds. For air-drying alkyds tung oil fatty acids are not so simple in manipulation as those from linseed, soya or dehydrated castor oil and are not produced in large quantities. Linseed oil fatty acids are used, in addition, for the manufacture of the fused type of linoleate driers, and in small amounts they have a useful peptising action on metallic drying soaps during fusion, and after their subsequent conversion to

terebines. The fatty acids from wool fat are used with naphthenic acid for the preparation of metal salts for use as driers.

Oxalic Acid

This acid is used in the manufacture of spirit varnishes containing rosin, spirit Manila or shellac, and its function is to effect decoloration. Small additions up to 1 per cent are used. Sometimes the bleached varnish exhibits a faint opalescence which may necessitate filtration.

Benzoic Acid

Like linseed oil fatty acids, benzoic acid is a valuable peptising agent. It is often added to metallic soaps, particularly cobalt and manganese naphthenates, to facilitate fusion on heating. Weight for weight it is stronger in action than linseed oil fatty acids and fractional percentage additions are adequate for satisfactory effects.

The addition of benzoic acid to alkyd varnishes containing lead driers is claimed to prevent precipitation of driers, and while it has this effect, it is generally not permanent.

Benzoic acid is sometimes added to enamel media for use with zinc oxide, and under these conditions, even with heavily pigmented enamels, the improvement in flow thus induced is very marked. A convenient form of addition of benzoic acid to pigmented products is as paste with linseed stand oil.

α-Crotonic Acid

Crotonic acid also is sometimes used to improve the flow of enamels.

Phthalic Anhydride

Phthalic anhydride is used, almost exclusively, in the varnish trade, in the manufacture of alkyd resins or dehydrated castor oil. Anhydride of reliable quality is readily obtained either in the form of long needle crystals or as flakes, and both forms are widely used. The needle form is less convenient to handle, being very bulky and requiring much space both during storage and in the initial stages in the reaction vessel. It does, however, disperse more homogeneously throughout the reactants and has not the tendency to settle at the bottom of the reaction vessel like the flakes.

Phthalic anhydride is sometimes dissolved in lacquers so that on evaporation of the solvents the anhydride forms large crystals to provide a pleasant crystalline effect.

Petrex

Petrex is the trade name of an organic acid which possesses the chemical name, 3-isopropyl-6-methyl-3, 6-endoethylene Δ^4 tetrahydro phthalic anhydride. The commercial product is not, however, strictly monomeric. Experimental evidence indicates that polymers of the acid are present also.

It is designed primarily as a phthalic anhydride substitute for alkyd resins, and is easier to use in that it does not sublime at resin-making temperatures.

It will be seen from its formula (p. 74) that it is a terpenic material, and it is because of this that resins made from it have good solvent properties. Petrex itself is soluble in aliphatic and aromatic hydrocarbons, drying oils, alcohols and esters.

The manufacture, modification and uses of Petrex are covered by a series of American Patent Specifications.

Maleic Anhydride

This is used exclusively in the manufacture of synthetic materials. It is a fundamental raw material in the manufacture of maleic anhydride resins, in conjunction with rosin, and of alkyds resins. It also yields interesting reaction products with tung oil.

Precautions must be taken in working with this material, for although it is supplied in solid form and is easy to handle, it volatilises readily at and below resin making temperatures. The vapours are very strong eye-irritants, and the author has personally experienced great discomfort and temporary distortion of vision through contact with them.

Naphthenic Acid

This is considered in detail in the chapter devoted to Driers and Metallic Soaps.

Citric Acid

This acid is added to spirit varnishes based on Manila copal, when they are used as media for pigmenting with pigments which have a feeding tendency. Thus lithopone which often contains traces of zinc oxide may feed with spirit Manila. The presence of citric acid is effective in preventing this or in reducing the stoutening after it has occurred.

REFERENCE

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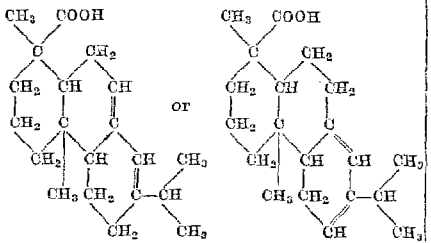
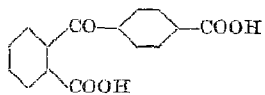
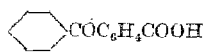
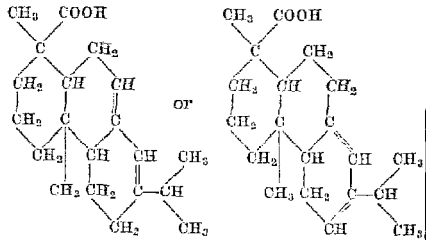
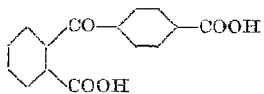
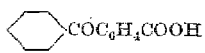
CONSTANTS OF ACIDS

Acid.	Formula.	M.Wt.	M.Pt. (°C.).	B.Pt. (°C.).	S.G.	A.V.	I.V.	Reference.
Almond oil (mixed f.a.)	—	—	13–14	—	—	—	100	—
Apricot kernel (mixed f.a.)	—	289	12–14	—	—	194·2	103	—
Arachis oil (mixed f.a.)	—	282	31–32	—	0·846 (99° C.)	199·0	94	—
Acetic	CH_3COOH	60·0	16	118	1·054 (16° C.)	934·0	—	—
Azelaic	$COOH(CH_2)_7COOH$	188·25	106	237/15 mm.	—	595·5	—	—
Adipic	$COOH(CH_2)_4COOH$	146·1	151	216/15 mm.	—	767·0	—	—
Acrylic	$CH_2{=}CHCOOH$	72·05	12	140	1·062 (13° C.)	779·0	—	—
Aconitic	$COOHCH{=}C(COOH)CH_2COOH$	174·08	191	—	—	965	—	—
Arachidic	$CH_3(CH_2)_{18}COOH$	312·3	77	205/1 mm.	—	179·6	—	—
Arachidonic	$C_{19}H_{31}COOH$ (probable)	304·2	—	—	—	184·4	333·7	7
Abietic (see also rosin)		302·5	80 (begins to soften)	—	—	185·5	—	16
Benzoic	C_6H_5COOH	122·09	121	249	1·201 (21° C.)	460·0	—	—
Butyric *n*	$CH_3(CH_2)_2COOH$	88·08	−8	163	0·9580 (14° C.)	637·0	—	—

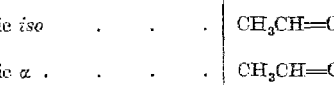
Butyric *iso*	$(CH_3)_2CHCOOH$	88·08	—47	155	0·948 (20° C.)	637·0	—	—
Brassidic	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$	338·64	65	282/30 mm.	0·858 (57° C.)	165·7	75·15	—
Behenic	$CH_3(CH_2)_{20}COOH$	340·35	81	306/60 mm.	—	164·8	—	—
Benzophenone 2 : 4′ dicarboxylic		270·25	—	—	—	415·0	—	—
Benzoyl benzoic		226·24	—	—	—	248·0	—	—
Brassylic	$COOH(CH_2)_{11}COOH$	244·37	112	—	—	459	—	—
Behenolic	$CH_3(CH_2)_7C{\equiv}C(CH_2)_{11}COOH$	336·62	57·5	—	—	166·7	—	—
Benzilic	$(C_6H_5)_2C(OH)COOH$	228	150	—	—	—	—	—
Coconut (mixed f.a.)	—	211	23–27	—	0·855 (99° C.)	266·0	9·7	—
Cod-liver oil (mixed f.a.)	—	288	20–23	—	—	194·6	144–174	—
Candlenut oil (mixed f.a.)	—	—	20–21	—	—	—	167	—
Cotton oil (mixed f.a.)	—	275	34–38	—	0·8407 (99° C.)	204·0	105–112	—
Croton oil (mixed f.a.)	—	285	—	—	—	196·7	111	—
Curcas oil (mixed f.a.)	—	—	24–26	—	—	—	105	—
Castor oil (mixed f.a.)	—	306	3–13	—	0·896 (99° C.)	183·4	89	—
Caproic	$C_5H_{11}COOH$	116·13	—2	205	0·929 (20° C.)	483·0	—	—
Caproic *iso*	$C_5H_{11}COOH$	116·13	—35	208	0·924 (20° C.)	483·0	—	—
Caprylic	$CH_3(CH_2)_6COOH$	144·12	16	237	0·917 (15° C.)	389·0	—	—

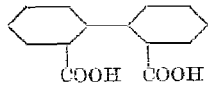
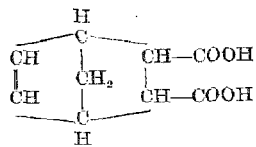
CONSTANTS OF ACIDS

Acid.	Formula.	M.Wt.	M.Pt. (°C.).	B.Pt. (°C.).	S.G.	A.V.	I.V.	Reference.
Almond oil (mixed f.a.)	—	—	13–14	—	—	—	100	—
Apricot kernel (mixed f.a.)	—	289	12–14	—	—	194·2	103	—
Arachis oil (mixed f.a.)	—	282	31–32	—	0·846 (99° C.)	199·0	94	—
Acetic	CH_3COOH	60·0	16	118	1·054 (16° C.)	934·0	—	—
Azelaic	$COOH(CH_2)_7COOH$	188·25	106	237/15 mm.	—	595·5	—	—
Adipic	$COOH(CH_2)_4COOH$	146·1	151	216/15 mm.	—	767·0	—	—
Acrylic	$CH_2{=}CHCOOH$	72·05	12	140	1·062 (16° C.)	779·0	—	—
Aconitic	$COOHCH{=}C(COOH)CH_2COOH$	174·08	191	—	—	965	—	—
Arachidic	$CH_3(CH_2)_{18}COOH$	312·3	77	205/1 mm.	—	179·6	—	—
Arachidonic	$C_{19}H_{31}COOH$ (probable)	304·2	—	—	—	184·4	333·7	7
Abietic (see also rosin)		302·5	80 (begins to soften)	—	—	185·5	—	16
Benzoic	C_6H_5COOH	122·09	121	249	1·201 (21° C.)	460·0	—	—
Butyric *n*	$CH_3(CH_2)_2COOH$	88·08	−8	163	0·9580 (14° C.)	637·0	—	—

Butyric *iso*	$(CH_3)_2CHCOOH$	88·08	−47	155	0·948 (20° C.)	637·0	—	—
Brassidic	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$	338·64	65	282/30 mm.	0·858 (57° C.)	165·7	75·15	—
Behenic	$CH_3(CH_2)_{20}COOH$	340·35	81	306/60 mm.	—	164·8	—	—
Benzophenone 2 : 4′ dicarboxylic . .		270·25	—	—	—	415·0	—	—
Benzoyl benzoic . . .		226·24	—	—	—	248·0	—	—
Brassylic	$COOH(CH_2)_{11}COOH$	244·37	112	—	—	459	—	—
Behenolic	$CH_3(CH_2)_7C{\equiv}C(CH_2)_{11}COOH$	336·62	57·5	—	—	166·7	—	—
Benzilic	$(C_6H_5)_2C(OH)COOH$	228	150	—	—	—	—	—
Coconut (mixed f.a.) . .	—	211	23–27	—	0·835 (99° C.)	266·0	9·7	—
Cod-liver oil (mixed f.a.) .	—	288	20–23	—	—	194·6	144–174	—
Candlenut oil (mixed f.a.) .	—	—	20–21	—	—	—	167	—
Cotton oil (mixed f.a.)	—	275	34–38	—	0·8467 (99° C.)	204·0	105–112	—
Croton oil (mixed f.a.) . .	—	285	—	—	—	196·7	111	—
Cureas oil (mixed f.a.) . .	—	—	24–26	—	—	—	105	—
Castor oil (mixed f.a.) . .	—	306	3–13	—	0·896 (99° C.)	183·4	89	—
Caproic	$C_5H_{11}COOH$	116·13	−2	205	0·929 (20° C.)	483·0	—	—
Caproic *iso*	$C_5H_{11}COOH$	116·13	−35	208	0·924 (20° C.)	483·0	—	—
Caprylic	$CH_3(CH_2)_6COOH$	144·12	16	237	0·917 (15° C.)	389·0	—	—

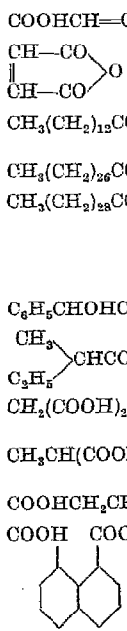
CONSTANTS OF ACIDS—*Continued*

Acid.	Formula.	M.Wt.	M.Pt. (°C.).	B.Pt. (°C.).	S.G.	A.V.	I.V.	Reference
Caprie	$CH_3(CH_2)_8COOH$	172·15	31	269	0·886 (40° C.)	326·0	—	—
Crotonic *iso*	$CH_3CH{=}CHCOOH$	86·07	14	169 decomp.	1·031 (15° C.)	652·0	—	—
Crotonic α	$CH_3CH{=}CHCOOH$	86·07	72	189	1·018	652·0	—	—
Citraconic	$COOHCH{=}C(CH_3)COOH$	130·08	80	—	1·616	862·0	—	—
Cinnamic	$C_6H_5CH{=}CHCOOH$	148·11	133	299	1·249	378·5	—	—
Citric	$COOHC(OH)(CH_2COOH)_2+H_2O$	210·11	100 *a.* 154	decomp.	1·542	801·0	—	—
Chaulmoogric		280·2	68	248/20 mm.	—	200·2	90·6	—
Chupanodonic	$CH_3(CH_2)_2C{\equiv}C(CH_2)_5CH{=}CH(CH_2)_2CH{=}CHCH_2CH{=}CH(CH_2)_2COOH$	330·3	—	—	—	169·8	368·11	4
Cerotic	$CH_3(CH_2)_{24}COOH$	396·4	89	—	—	141·6	—	—
Camphoric	$C_8H_{14}(COOH)_2$	200·26	187	—	—	560·0	—	—
Coumaric	$OHC_6H_4CH{=}CHCOOH$ 1 : 2	164	207	—	—	—	—	—
Carnaubic	$C_{24}H_{48}O_2$	368	—	—	—	152·4	—	—
Dehydrated castor (mixed f.a.)	—	280	—	—	0·906 (15·5° C.)	200	—	—
Daturic	$CH_3(CH_2)_{15}COOH$	270·51	59·5	—	—	207·4	—	1
Dihydroxystearic 9. 10	$CH_3(CH_2)_7CH(OH)CH(OH)(CH_2)_7COOH$	316·54	133	—	—	177·2	—	—
Dihydroxybehenic 13. 14	$CH_3(CH_2)_7CH(OH)CH(OH)(CH_2)_{11}COOH$	372·66	132	—	—	150·4	—	—
Doeglic	$C_{19}H_{36}O_2$	296·55	—	—	—	189·1	85·81	2
Diglycollic	$COOHCH_2OCH_2COOH$	134·1	—	—	—	836·0	—	—

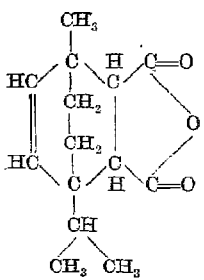
Diphenic		242·08	228	sublimes.	—	462·5	—	—
Elaeostearic α	$CH_3(CH_2)_3(CH{=}CH)_3(CH_2)_7COOH$	278·25	49	235/12 mm.	—	201·5	273·7	—
Elaeostearic β	—	278·25	71	—	—	201·5	—	—
Erucic	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$	338·64	33	281/30 mm.	0·860 (55° C.)	165·8	75·15	—
Elaidic	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	282·37	51	225/10 mm.	—	198·8	90·07	—
Endomethylene Δ^4 tetrahydrophthalic 3. 6		182·19	—	—	—	615·0	—	—
Ethyl malonic	$C_2H_5CH(COOH)_2$	132	111	160 decomp.	—	848	—	—
Formic	HCOOH	46·03	8	100	1·245 (0° C.)	1217·0	—	—
Fumaric	COOHCH=CHCOOH	116·05	200 sublimes.	—	1·635 (20° C.)	967·0	—	—
Gadoleic	Probably $\Delta 9:10$ eicosenoic	—	24·5	—	—	—	—	—
Glutaric	$COOH(CH_2)_3COOH$	132·09	97	303	—	849	—	—
Glycoleic	$CH_2OHCOOH$	76·04	79	decomp.	—	738	—	—
Gallic	$(OH)_3C_6H_2COOH$	170·13	220 decomp.	—	1·694 (4° C.)	329·6	—	—
Gorlic	$C_{18}H_{36}O_2$	278·2	—	—	—	201·7	181·1	—
Hyndocarpic	$C_{16}H_{28}O_2$	252·2	60	—	—	222·3	100·6	—
Hypogoeic	$CH_3(CH_2)_7CH{=}CH(CH_2)_5COOH$ (probable)	254·46	33	236/15 mm.	—	220·5	100	5
Heptylic	$CH_3(CH_2)_5COOH$	130·21	−10	223	0·922 (15° C.)	431·0	—	—

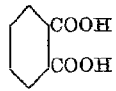
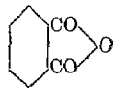
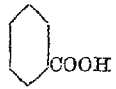
CONSTANTS OF ACIDS—*Continued*

Acid.	Formula.	M.Wt.	M.Pt. (°C.).	B.Pt. (°C.).	S.G.	A.V.	I.V.	Reference.
Herring oil (mixed f.a.)	—	292	—	—	—	192·0	130	—
Hempseed oil (mixed f.a.)	—	—	18–19	—	—	—	149	—
Hydrocinnamic	$C_6H_5CH_2CH_2COOH$	150	48	280	1·071 (49° C.)	374	—	—
Hydroxybenzoic *m*	HOC_6H_4COOH 1. 3	138	200	—	1·473 (4° C.)	—	—	—
Hydroxybenzoic *p*	HOC_6H_4COOH 1. 4	138	213	—	1·443 (20° C.)	—	—	—
Isanic	$C_{13}H_{19}COOH$ (probable)	220·34	41	—	—	254·8	461·8	6
Itaconic	$COOHC(=CH_2)CH_2COOH$	130·11	161	—	1·632	862·0	—	—
Juniperic	$CH_2(OH)(CH_2)_{14}COOH$	272·48	95	—	—	206·0	—	8
Jecoleic	$C_{19}H_{36}O_2$	296·55	—	—	—	189·2	85·8	9
Japanese fish oil (mixed f.a.)	—	—	15–28	—	—	—	120–180	—
Linseed (mixed f.a.)	—	283	17–24	—	0·8612 (99° C.)	198	179–210	—
Lauric	$CH_3(CH_2)_{10}COOH$	200·1	44	180/16 mm.	0·875 (44° C.)	280·5	—	—
Lignoceric	$CH_3(CH_2)_{22}COOH$	368·4	86	—	0·8207	152	—	—
Lanopalmic	$C_{16}H_{22}O_3$	272·48	—	—	—	—	—	—
Lanoceric	$C_{29}H_{57}(OH)_2COOH$	484·9	104	—	—	116	—	—
Linusic	$C_{17}H_{29}(OH)_6COOH$	380·54	204	—	—	147·3	—	—
Lactic	$CH_3CH(OH)COOH$	90·07	18	119/12 mm.	—	623	—	—
Linolenic	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$	278·25	—	230/17 mm.	—	201·6	273·7	—

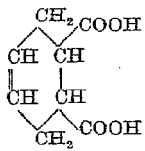
Linoleic	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	280·25	—	228/14 mm.	—	200·2	181·1	—
Licanic α	$CH_3(CH_2)_3(CH{=}CH)_3(CH_2)_4CO(CH_2)_2COOH$	290·2	74	—	—	193·2	—	—
Licanic β	—	290·2	96·5	—	—	193·2	—	—
Levulinic	$CH_3CO(CH_2)_2COOH$	116	37	245 decomp.	1·1395 (20° C.)	483·6	—	—
Maleic	$COOHCH{=}CHCOOH$	116·05	130	decomp.	1·59	967	—	—
Maleic anhydride	$\begin{matrix} CH{-}CO \\ \| \\ CH{-}CO \end{matrix}\!\!>\!O$	98·06	56	202	0·934 (20° C.)	1143	—	—
Myristic	$CH_3(CH_2)_{12}COOH$	228·2	53	199/16 mm.	0·858 (60° C.)	245·8	—	—
Montanic	$CH_3(CH_2)_{26}COOH$	424·84	83	—	—	132·2	—	10
Melissic	$CH_3(CH_2)_{28}COOH$	452·9	91	—	—	124·0	—	—
Menhaden oil (mixed f.a.)	—	289	—	—	—	194	163	—
Maize oil (mixed f.a.)	—	283	18–21	—	0·8529 (99° C.)	198·3	122	—
Mandelic	$C_6H_5CHOHCOOH$	152	118 *dl.*	1·361 (4° C.)	—	369	—	—
Methyl ethyl acetic	$\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!CHCOOH$	102	< −80	174	0·941 (20° C.)	550	—	—
Malonic	$CH_2(COOH)_2$	104	133	—	1·631 (15° C.)	1079	—	—
Methyl malonic	$CH_3CH(COOH)_2$	118	135 decomp.	—	1·455 (20° C.)	949	—	—
Malic	$COOHCH_2CH(OH)COOH$	134	100	—	1·595	837	—	—
Naphthalic 1. 8		216·2	270 decomp.	—	—	518·0	—	—
α-Naphthoic	$C_{10}H_7COOH$	172	160	300	—	326·2	—	—

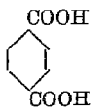
CONSTANTS OF ACIDS—*Continued*

Acid.	Formula.	M.Wt.	M.Pt. (°C.).	B.Pt. (°C.).	S.G.	A.V.	I.V.	Reference.
β-Naphthoic	$C_{10}H_7COOH$	172	182	>300	1·077 (100° C.)	326·2	—	—
Niger oil (mixed f.a.)	—	—	22–28	—	0·857 (99° C.)	—	135	—
Naphthenic	—	—	—	150–190 13 mm.	0·950 (15° C.)	230–250 170 (special grade)	—	—
Olive (mixed f.a.)	—	286	24–28	—	0·843 (99° C.)	196	86	—
Oleic	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	282·37	14	223/10 mm.	0·898 (14° C.)	198·8	90·07	—
Oxalic (anhydrous)	COOH . COOH	90·04	189	—	—	1246	—	—
Oxalic (hydrous)	$C(OH)_3 . C(OH)_3$	126·06	101	—	1·63	890·0	—	—
Perilla oil (mixed f.a.)	—	284	5	—	—	—	211	—
Palmitic	$CH_3(CH_2)_{14}COOH$	256·34	62	278/100 mm.	0·846 (8° C.)	218·8	—	—
Petrex, 3-isopropyl-6-methyl-3, 6-endoethylene Δ^4 tetra hydro- phthalic anhydride		215	40–50	—	1·50	530 approx.	—	—
Propionic	CH_3CH_2COOH	74·07	−22	140	0·996 (19° C.)	757·5	—	—

Phthalic-*o*		166·09	195 decomp.	—	1·585	675·0	—	—
Phthalic anhydride		148·07	130	284	1·53	758·0	—	—
Phthalic *iso*		166·09	>300	—	—	675·0	—	—
Petroselinic	$CH_3(CH_2)_{10}CH{=}CH(CH_2)_4COOH$	282·3	30–33	—	—	198·6	90·07	11
Petroselenolic	$CH_3(CH_2)_{10}C{\equiv}C(CH_2)_4COOH$	280·5	45	—	—	200·0	—	12
Pelargonic	$CH_3(CH_2)_7COOH$	158·27	12	253	0·909 (15° C.)	354·5	—	—
Parinaric	$C_{18}H_{28}O_2$	274·2	83·5	—	—	204·5	372·4	—
Poppyseed (mixed f.a.)	—	281	20–21	—	0·857 (99° C.)	199·7	139·0	—
Protocatechuic	$(OH)_2C_6H_3COOH$	154	194 decomp.	—	1·542 (4° C.)	—	—	—
Phenyl acetic	$C_6H_5CH_2COOH$	136	76	262	1·228 (20° C.)	412·5	—	—
Pimelic	$C_5H_{10}(COOH)_2$	160	103	272/100 mm. sublimes	1·329 (15° C.)	701	—	—
Pyruvic	$CH_3COCOOH$	88	13	165	—	638	—	—
Ricinoleic	$CH_3(CH_2)_5CH(OH)CH_2CH{=}CH(CH_2)_7COOH$	298·3	4	—	0·9509 (15° C.)	188·0	85·1	—
Ricinelaidic	$CH_3(CH_2)_5CH(OH)CH_2CH{=}CH(CH_2)_7COOH$	298·3	52	—	—	188·0	85·1	—
Ricinostearolic	$CH_3(CH_2)_5CH(OH)CH_2C{\equiv}C(CH_2)_7COOH$	296·5	51	—	—	—	—	—
Rosin	—	—	—	—	1·075 (15° C.)	164	110	—

CONSTANTS OF ACIDS—*Continued*

Acid.	Formula.	M.Wt.	M.Pt. (°C.).	B.Pt. (°C.).	S.G.	A.V.	I.V.	Reference.
Ravison oil (mixed f.a.)	—	—	—	—	—	—	126	—
Rape oil (mixed f.a.)	—	320	18–19	—	0·8438 (99° C.)	175·2	102	—
Rice oil (mixed f.a.)	—	289	32–36	—	—	194·0	97	—
Salicylic	HOC_6H_4COOH 1. 2	138·09	155	sublimes	1·443	406·3	—	—
Stearic	$CH_3(CH_2)_{16}COOH$	284·37	69	291/100 mm.	0·852 (70° C.)	197·2	—	—
Sabinic	$CH_2(OH)(CH_2)_{16}COOH$	216·36	—	—	—	259·2	—	13
Sativic	$C_{17}H_{31}(OH)_4COOH$	348·54	173	—	—	161·0	—	—
Stearolic	$CH_3(CH_2)_7C{\equiv}C(CH_2)_7COOH$	280·50	48	260	—	200·0	—	—
Suberic	$COOH(CH_2)_6COOH$	174·15	140	300	—	644·0	—	—
Sebacic	$COOH(CH_2)_8COOH$	202·19	133	295/100 mm.	—	554·5	—	—
Succinic	$COOH(CH_2)_2COOH$	118·07	185	235	1·552	950·0	—	—
Stearidonic	$C_{18}H_{28}O_2$ (probable)	276·2	—	—	—	203·0	—	—
Seal oil (mixed f.a.)	—	292	22–23	—	—	192·0	143	—
Soya bean oil (mixed f.a.)	—	—	26–29	—	—	—	132	—
Sunflower oil (mixed f.a.)	—	280	22–24	—	—	200·5	134	—
Sesamé oil (mixed f.a.)	—	286	23–26	—	—	196·0	106–111	—
Salmon oil (mixed f.a.)	—	—	—	—	—	—	169	—
Tetrahydrophthalic		170·18	—	—	—	659·0	—	—
Tariric	$CH_3(CH_2)_{10}C{\equiv}C(CH_2)_4COOH$	280·25	50	—	—	200·25	181·1	14

Tiglic	$CH_3CH{=}C(CH_3)COOH$	100	64	198·5	0·872 (20° C.)	561·0	254	15
Tung oil (mixed f.a.)	—	297	38–40	—	—	188·8	168	—
Terephthalic		166·09	—	sublimes	—	675·0	—	—
Toluic *o*	$CH_3C_6H_4COOH$ 1. 2	136	102	259	—	412·5	—	—
Toluic *m*	$CH_3C_6H_4COOH$ 1. 3	136	109	263	—	412·5	—	—
Toluic *p*	$CH_3C_6H_4COOH$ 1. 4	136	177	275	—	412·5	—	—
Tannic	$C_{14}H_{10}O_9 + [2H_2O]$	322	200–220 decomp.	—	—	—	—	—
Trimethyl acetic	$(CH_3)_3C\,.\,COOH$	102	35·5	164	0·905 (50° C.)	550	—	—
Tridecylic	$CH_3(CH_2)_{11}COOH$	214	51 —	236/100 mm.	—	262	—	—
Tartaric	$COOHCH(OH)CH(OH)COOH$	150	169 d.	—	1·7598 (20° C.)	748	—	—
Undecylic	$CH_3(CH_2)_9COOH$	186	29	228/160 mm.	—	302	—	—
Valeric	$CH_3(CH_2)_3COOH$	102·11	−59	186	0·940 (19° C.)	549·0	—	—
Valeric *iso*	$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CHCH_2COOH$	102·11	−51	176	0·931 (20° C.)	549·0	—	—
Whale oil (mixed f.a.)	—	290	24–27	—	0·860 (99° C.)	193·4	120	—
Walnut oil (mixed f.a.)	—	—	16–20	—	—	—	150	—

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CHAPTER 3

MONOGLYCERIDES

Preparation

THE monoglycerides of drying oils provide a new and very useful addition to the range of raw materials for varnish manufacture. They occur naturally, only in small quantities, but are readily synthesised. Monoglycerides may be represented by the general formulæ

$$\begin{array}{l} CH_2OH \\ | \\ CH\ OH \\ | \\ CH_2OOC\,.\,R \end{array} \quad \text{or} \quad \begin{array}{l} CH_2OH \\ | \\ CHOO\ C\,.\,R \\ | \\ CH_2OH \end{array}$$

Their manufacture has attracted considerable attention and has been summarised by Mundy.[1]

α-Monoglyceride can be made by heating α-monochlorhydrin and the sodium salt of a fatty acid.[2] Methods of this type are beyond the available facilities of the average varnish maker, but he can obtain satisfactory products directly from drying oils or the fatty acids derived therefrom.

Mono and/or diglycerides are prepared by heating fatty acids and glycerol with the metallic glycerates of an alkali or an alkaline earth metal having at least one free hydroxyl, at 100°–200° C.,[3] or by heating fatty acids or mixtures with oil, with glycerol at 200°–220° C. One per cent of a glycerate is claimed to catalyse this latter reaction.[3] Although described as glycerates it is probable the substances referred to are glyceroxides, i.e. the reaction products of metallic compounds with glycerol, and not the salts of glyceric acid. In the reaction between fatty acids and glycerol, mixed mono-, di- and tri-glycerides are formed. The reaction is facilitated by removing the water eliminated under vacuum, and by the presence of aromatic sulphonic acids.[4] It has been demonstrated also elsewhere that the rapid removal of water either by the passage of an inert gas [5] or by means of anhydrous copper sulphate favours the formation of monoglycerides. High yields of monoglyceride (90 per cent) at 120°–180° C. are possible, if the reaction is catalysed by the presence of camphor-β-sulphonic acid, with phenol or cresol as a mutual solvent for the reactants.[6] The formation of monoglycerides is facilitated if the fatty acids are heated with a large excess of glycerol.[7] In an example 100 parts of linseed fatty acids are heated at 200°–250° C. with 92 parts of glycerol. Preparation of monoglyceride by this method is useful only for the subsequent preparation of alkyd resins by reason of the large excess of free glycerol. Some methods involve the use of glycerol equivalent to ten times the weight of fatty acid; the mixture being heated at 170°–180° C.

If polyglycerols are substituted for glycerol the speed of reaction

with fatty acids is increased considerably.[8] Polyglycerols may be prepared by heating glycerol with sodium hydroxide at 280° C.

The cheapest and most convenient method of synthesis of monoglycerides is by the direct interaction of drying oils and glycerol. One protected method describes a reaction between these ingredients at 200°–250° C. for one to ten hours, using a little monoglyceride as an accelerating agent. It is generally accepted that the presence of traces of alkaline substances promote the interchange. Potassium carbonate, lime,[9, 10] caustic soda, and disodium hydrogen phosphate, have been used successfully. When used in effective quantities they have the disadvantage of causing discoloration. Certain metallic oxides, e.g. alumina, thoria, and tin and titanium oxides have been used also, as well as their soaps.[11]

Alternatively, linseed oil and glycerol are heated in an inert atmosphere at 170°–180° C. for three hours and the temperature raised finally to 230° C.[12] Two hours' treatment at 250°–280° C. in the presence of approximately 0·005 per cent of calcium glycerate, yields a product satisfactory for use in alkyd resins.[13]

Tung oil mixed glycerides may be obtained by heating the tung oil to 235° C. and adding glycerol slowly. The treatment is continued until the mixture becomes clear.[14] Another method raises the temperature to 280° C. for incorporation.[15] Mundy [1] describes a satisfactory method for the production of monoglycerides applicable to all the common drying oils including linseed, perilla, soya bean, dehydrated castor and linseed-tung oil blends. Yields of 96–100 per cent are claimed. The reaction, which is self-catalysed, consists in heating the oil-glycerol mixture in an inert atmosphere at 290° C. approximately. The application of a slightly reduced pressure aids the removal of water.

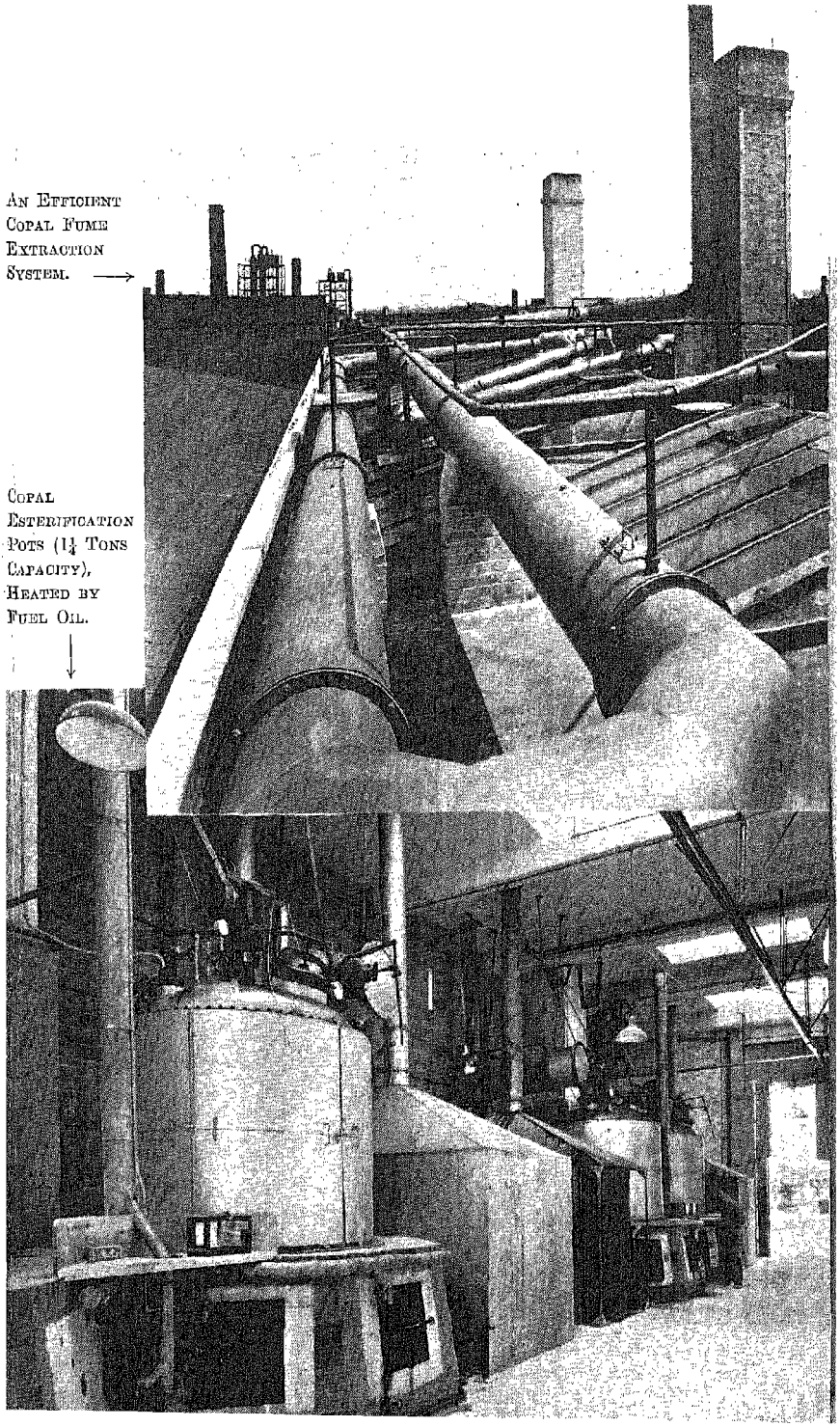
Partial hydrolysis stimulated by the action of enzymes is another method of monoglyceride formation.

Polymerised oils also react with glycerol to yield monoglycerides.

The alcoholysis of drying oil fatty acids with other polyhydric alcohols has been explored by Drinberg and Blagonravova.[16] Monohydric alcohols such as amyl alcohol yield products which do not dry. The esters of glycols (ethylene and propylene) yield products with semi-solid films. The products of alcoholysis of linseed oil and ethylene glycol are stated elsewhere to have good drying properties. Mannitol and glycerol yield esters with fatty acids, comparable in speed of dry with the natural oils, but pentaerythritol esters yield films of improved hardness and dry.

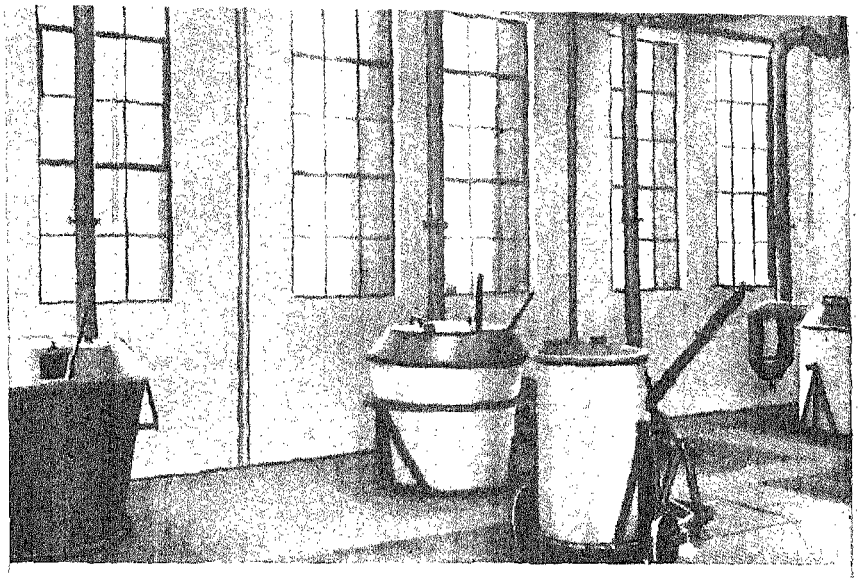
Yields of 85–95 per cent of alkyl esters of drying oil fatty acids are claimed by heating the oil with an excess of monohydric aliphatic alcohol (i.e. two or three times the theoretical quantity). The liberated glycerol is separated by addition of hydrocarbons.[17]

Monoglycerides dry in the presence of the usual drying metals. With linseed monoglyceride the film is tacky, but tung oil monoglyceride

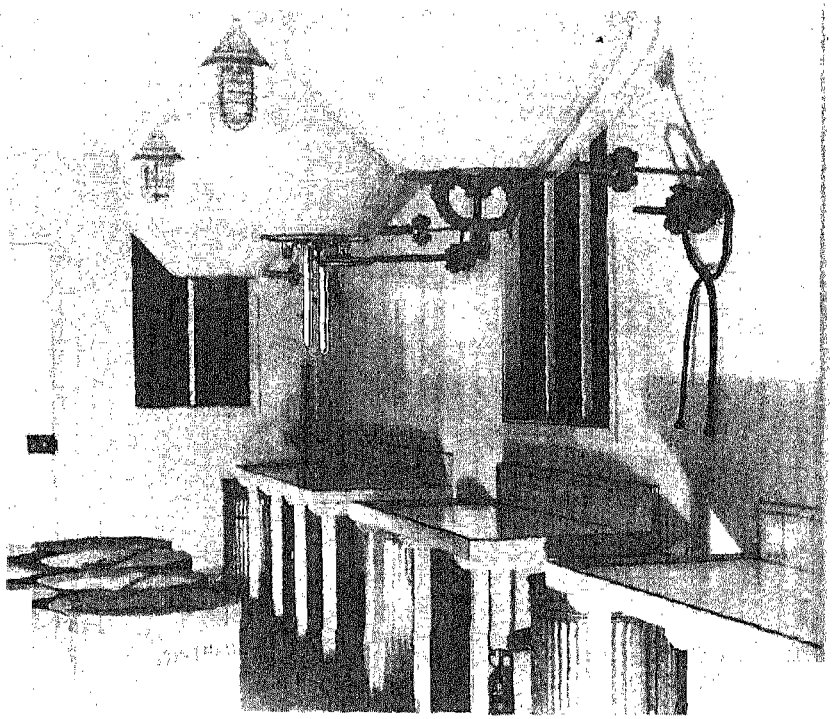


An Efficient Copal Fume Extraction System. →

Copal Esterification Pots ($1\frac{1}{4}$ Tons Capacity), Heated by Fuel Oil. ↓



TYPICAL VARNISH MAKING INSTALLATION.



POLYSTYRENE EXTRUSION HOUSE.

To face p. 81.

yields tack-free films. Prolonged heating of monoglyceride at elevated temperatures induces polymerisation but it is not very marked. When first prepared, monoglycerides of linseed oil are clear pale viscous oils. On standing they crystallise to a white pasty mass, sometimes with a clear supernatant oil.

Unchanged triglycerides may be removed from monoglycerides or mixtures with diglycerides, by extraction with alcohol, in which the two latter compounds dissolve. Dilution of the resultant solution with water causes separation of diglycerides.

Uses

The most important use of monoglycerides of the drying oils is in the manufacture of alkyd resins. Their properties, however, are such that many other valuable applications may be anticipated in the future. The monoglycerides of both linseed and dehydrated castor oils are used in large amounts in Great Britain. Their two reactive hydroxyl groups permit reactions with all acidic resins, and thus it is possible to make combination varnishes of low acidity with rosin and run congo. Red and yellow accroides, and dammar react similarly. Mundy has shown that at a temperature of 288° C. a mixed rosin-linseed ester of acid value 5·0 can be obtained after ninety minutes' treatment. In a similar way a mixed run congo-linseed ester would provide the basis for a useful hard gloss medium of low acidity for use with all types of pigment. Products of very high exterior durability have also been produced by the same worker from monoglycerides and the principal acid of Kauri gum-agathic acid.[18]

Monoglycerides react also with shellac on heating, to yield combinations which are soluble in white spirit. This subject is dealt with in greater detail under "Shellac." Unlike the drying oils from which they are derived monoglycerides are soluble in ethyl alcohol, and since they are readily miscible with shellac and Manila they act as satisfactory plasticisers. The reaction product from linseed oil monoglycerides and oxidised rosin is claimed to be soluble in mineral spirits if lengthened with linseed oil, and the resultant varnish is said to have superior durability to a similar varnish using either rosin ester or copal ester. Oxidised rosin, itself, is insoluble in mineral spirits.

Monoglycerides act also as emulsifying agents for oil-water emulsions.

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CONSTANTS OF MONOGLYCERIDES

Monoglyceride.	Formula.	M.Wt.	M.Pt. (° C.).	B.Pt. (° C.).	S.G.	S.V.	I.V.	A.V.
Monolinolin . . .	$C_3H_5\begin{cases}C_{17}H_{31}COO\\(OH)_2\end{cases}$	354·6	—	—	—	158·5	[143·5]	— *
Monolinolenin	$C_3H_5\begin{cases}C_{17}H_{29}COO\\(OH)_2\end{cases}$	352·6	—	—	—	159·4	—	— *
Linseed oil monoglyceride	—	—	—	—	0·982 (30° C.) 0·988 (15° C.)	166·0 162·4	—	1·8 2·8 *
Dehydrated castor oil monoglyceride . .	—	—	—	—	—	176·4	—	3·1 *
Mixed linseed-tung oil monoglycerides 3 : 1 .	—	—	—	—	0·990	165·3	—	1·7 *
α-Monoacetin . .	$C_3H_5\begin{cases}CH_3COO\\(OH)_2\end{cases}$	134·1	Liquid	130°/2 mm.	1·2212 (15° C.)	418·0	—	—
α-Monobutyrin . .	$C_3H_5\begin{cases}C_3H_7COO\\(OH)_2\end{cases}$	162·2	Liquid	270°	1·008 (17° C.)	346·0	—	—
α-Monoformin . .	$C_3H_5\begin{cases}H\,.\,COO\\(OH)_2\end{cases}$	120·1	Liquid	165° (vacuum)	—	467·0	—	—
α-Monoisovalerin . .	$C_3H_5\begin{cases}C_4H_9COO\\(OH)_2\end{cases}$	176·2	Liquid	—	1·00 (16° C.)	318·2	—	—

* Mundy, *J.O.C.C.A.*, 1938, **21**, 101.

CONSTANTS OF MONOGLYCERIDES—*Continued*

Monoglyceride.	Formula.	M.Wt.	M.Pt. (° C.).	B.Pt. (° C.).	S.G.	S.V.	I.V.	A.V.
α-Monomelissin . .	$C_3H_5\begin{cases}C_{29}H_{59}COO\\(OH)_2\end{cases}$	526·9	92°	—	—	106·5	—	—
α-Mono-olein . . .	$C_3H_5\begin{cases}C_{17}H_{33}COO\\(OH)_2\end{cases}$	356·6	35°	—	0·947 (21° C.)	157·4	71·4	—
α-Monostearin . .	$C_3H_5\begin{cases}C_{17}H_{35}COO\\(OH)_2\end{cases}$	358·3	81° / 73°	—	0·984 (20° C.)	156·6	—	—
α-Monopalmitin . .	$C_3H_5\begin{cases}C_{15}H_{31}COO\\(OH)_2\end{cases}$	330·3	77° / 72°	—	—	169·7	—	—
α-Monolaurin . .	$C_3H_5\begin{cases}C_{11}H_{23}COO\\(OH)_2\end{cases}$	274·2	63° / 59°	—	—	204·5	—	—
α-Monomyristin . .	$C_3H_5\begin{cases}C_{13}H_{27}COO\\(OH)_2\end{cases}$	302·5	68°	—	—	185·4	—	—
α-Monocerotin . .	$C_3H_5\begin{cases}C_{25}H_{51}COO\\(OH)_2\end{cases}$	471·5	79°	—	—	119·0	—	—
Monoricinolein . .	$C_3H_5\begin{cases}C_{17}H_{32}(OH).COO\\(OH)_2\end{cases}$	372·6	Liquid	—	1·028 (20° C.)	150·5	68·3	—

CHAPTER 4

NATURAL OIL VARNISH RESINS

ALTHOUGH much rapid progress has been made in the use of synthetic resins in the manufacture of varnishes and allied products, natural resins are used and will continue to be used in certain products for many years to come. So long as they retain their advantage of price they will continue to be used for normal decorative varnishes, paint and enamel media and for special purposes such as in cheaper silver stoving varnishes, etc. There is a marked tendency also for them to be used in conjunction with synthetic products. When they are used thus it may be by simple mixture or they may enter into actual chemical combination. Composite products are available which are derived from natural resins and alkyds, or from natural resins and phenol formaldehyde resins, to quote only two examples.

CONGO COPALS

Of all the natural copals available to-day, congo copals are by far the most widely used, and it is not surprising, therefore, that the greater part of recent research and development work has been conducted on this particular type.

Source.—Congo copal as its name implies is a fossil resin obtained from the Belgian Congo. The resin is dug out of the swampy ground. It is an exudation from *Copaifera demeusii* and *Liquidamba styrflua.*[1]

Production.—The resin as obtained is very dirty and is roughly cleaned. Then it is cleaned to a condition suitable for use by machines exploiting the cleansing action of a sand blast. Cleaning is also done by hand scraping. During the final cleaning, surface dirt and deep veins of dirt are removed as well as excessively fossilised resin. Highly fossilised resin is distinguished as an opaque white layer of resin which easily powders. It may be distinguished also, for highly fossilised resin has a much lower density than the normal varnish resin. It is quite valueless from the varnish maker's point of view.

The clean resin is then sorted in grades which vary in colour and size. The colour of the lumps may range from water-white to yellowish-brown or even reddish-brown.

Some pieces of copal are quite transparent and others are cloudy or milky. This milkiness is not necessarily a serious defect, for the resin usually runs normally. The colour of Congo copal may darken on ageing, but Hellinckx states that the discoloration is at the surface only and can be removed by washing with solvents.[2]

Grades.—The size varies from dust, through chips to quite bold lumps of several inches diameter. Dust has a tendency to insolubility and yields dark products after running. Chips comprise an assorted mixture

of various colours with some dust and dirt. Although they are more soluble than dust they run to give dark products. The best size of resin for running is uniform pieces of about one inch diameter. It is common practice for the varnish maker to reduce the size of large lumps by crushing. Large lumps are more difficult to run than the one-inch pieces in that they take longer to fuse, with consequent darkening. A large varnish maker may hold in stock up to ten or more different grades of Congo.

Composition.—According to Hellinckx Congo copal contains two acids, congocopalic acid ($C_{36}H_{58}(COOH)_2$), and congocopalolic acid, ($C_{21}H_{32}(OH)COOH$). The former is present to the extent of 43 per cent. In addition, resenes and essential oils like limonene are present.[2] Mertene fractionated Congo copal into α and β-resenes, α_1 and α_2-congocopalolic acids and essential oils.[3]

Hardness.—Natural copals vary widely in hardness, and the table on page 62 demonstrates the hardness of Congo in relation to other natural resins.

The melting-points of copals cover such extended ranges that any record of them would be of doubtful value.

The Running of Copals

When Congo, broken small, is placed in a gum-running pot and fierce heat applied the resin melts and undergoes decomposition, yielding an oil soluble product. This heating process is known as "gum running." Considerable experience is necessary to obtain the best results. Experienced workmen conduct both the running and oiling down processes without the aid of a thermometer. The quantity of copal run at a time varies considerably. Quantities used in this country are 56 lb., 60 lb., 80 lb., 100 lb., 112 lb., ½ ton and 1 ton. It is also probable that 5 and 10 ton batches are being run. A good varnish maker will handle two or three of the smaller batches simultaneously. Advantages showed for large-scale batches are paler products, smaller running losses, better homogeneity and greater production per man-hour. Since the product obtained by large batch operation tends to be paler, cheaper grades of copal can be used than would be possible with small-scale batches. The arguments in favour of large-scale operation are not so overwhelming as they appear at first sight, for much depends on the ability and skill of the varnish maker for output with small individual batches. The decision to instal plant for large batches is one which is controlled by local factors.

As soon as the heat is applied to the copal it must be kept on the move to avoid local overheating and charring, resulting in loss of colour and the possibility of flashing.

Modifications in the method of heating have been suggested to avoid overheating, with its consequent undesirable results. A plant is described involving the use of a jacketed aluminium kettle. The resin is melted

HARDNESS OF NATURAL OIL VARNISH RESINS

	Investigator.					
	Bottler (I).	Bottler (II).	Nicolardot and Coffignier (4).	Manning (5).	Wiesner.	Worlee.
Hardest	1. Zanzibar 2. Mozambique 3. Lindi 4. *Red Angola* 5. Pebble 6. Sierra Leone 7. Benguela 8. Cameroon 9. Congo 10. *Manila* 11. White Angola 12. Kauri 13. Sierra Leone (new) 14. Hymenoea	1. Zanzibar 2. Mozambique 3. Madagascar 4. *Sierra Leone* (fossil) 5. Red Angola 6. Benguela 7. Bastard Angola 8. Pebble 9. Accra 10. Benin 11. Loango 12. Gaboon 13. Congo 14. Sierra Leone (recent) 15. *White Angola* 16. Kauri 17. Manila 18. Borneo 19. Singapore 20. S. America 21. Brazil	1 { Zanzibar, *Madagascar*, Demerara 2 { *Congo*, Benguela, Cameroon, Angola Red, Brazil, Angola White, Manila, Sierra Leone 3 { *Pontianac*, Damar, Sandarac, Mastic	1. Congo 2. Kauri 3. Boea (Manila) 4. *Pontianac* 5. Loba (Manila) 6. Pale East India (Damar) 7. Black East India (Damar) 8. Batu Damar 9. Manilas 10. Singapore Damar 11. Batavia Damar 12. Mastic 13. Sandarac 14. Accroides 15. Elemi	1. Zanzibar 2. Mozambique 3. Sierra Leone 4. Gaboon 5. Angola 6. Benguela 7. Kauri 8. Manila 9. Courbaril	1 { Zanzibar, Sierra Leone, Benguela, Angola 2 { West Indian, Kauri, Manila, Accra (Zucker)

indirectly by means of a hot inert liquid which flows through the outer jacket of the kettle. Decomposition into fume is stated to be less than with the usual running process and the run copal is paler.[6] Kollin emphasises the importance of heat control in avoiding decomposition and cracking, in order to obtain products of superior characteristics.[7] As the resin melts considerable frothing occurs due to the evolution of volatile material. When the resin is run completely the frothing disappears and the molten resin runs cleanly from the stirrer. Temperatures achieved during running may be as high as 360° C. The experience of the expert gum runner is most evident in deciding precisely when the running process is complete. If the resin is run insufficiently it will demonstrate inferior oil compatibility and "floaters" or pieces of unrun resin may be found undispersed at the surface of the finished varnish after thinning. Processes have been described in which superheated steam is ejected into the copal during the running process. One advantage of this process is that products of exceptionally pale colour are obtained.[8]

If the resin is overrun, uneconomical losses of resin will occur as well as a proportionate darkening in colour. Congo, when run correctly, loses approximately 25 per cent by weight. This is a good average figure and will serve as the basis for formulation.

Barry and Dunster give a comprehensive list of running losses for the common copals. For Congo they give somewhat higher loss at 25–35 per cent. Manila has a similar loss of 25–35 per cent. Benguela, Pontianac and Angola lose 20–25 per cent; Zanzibar animi 15–20 per cent, Sierra Leone and Kauri 12–15 per cent.[9]

When the resin is run sufficiently, preheated varnish linseed oil is added gradually in small lots with vigorous stirring. After each addition the oil-resin mix is reheated, and the temperature maintained until the oil has been incorporated satisfactorily and some bodying has occurred, as evidenced by a "head" of froth which develops at the surface of the hot mix. Further similar additions of hot oil are made as required. The more a resin is run the more brittle it becomes.

Fumes of Copal Oils

The volatile matter distilling off during the running process is condensed and is described as "fumes." This is of very little value and is often disposed of as waste although attempts have been made to use it as fuel. It may be used as a thinner for cheap high temperature black stoving enamels, in driers, putty, wood preservatives, and shoe polishes. Varnish fumes, or copal oils, as they are sometimes described, are very complex. Fumes from Manila copal have yielded pinene, β-pinene, dipentene, limonene and camphene. Pinene has been detected in Kauri fumes. Sesquiterpenes, polyterpenes and acidic bodies are also present in copal fumes.[10] The presence of tetramethylhexahydronaphthalene has also been discovered.[11]

Copal oils are highly acidic, but the acidity can be reduced by esterifying with glycerol or by reacting with lime.

On chlorination, oils of increased viscosity are obtained. Their normally dark colours can be improved by bleaching with hypochlorite. After bleaching they may be used as plasticisers.[12]

English and Continental Gum Running.—Sleightholme draws attention to the difference between English and Continental practice in gum running. The English method involves the use of unpolymerised linseed oil which, on heating with the acidic resin, permits interesterification and liberates free oil fatty acids. With the Continental method polymerised oils are used and less interesterification occurs. Whilst interesterification is desirable for some purposes the liberation of oil fatty acids may cause feeding with basic pigment. Sleightholme suggests that the fatty acids could be distilled off with advantage.[13]

Copals and Monoglycerides.—Another method of producing varnishes from run copals is to heat the run copal with drying oil monoglyceride until interaction occurs. Varnishes of lower acidity are obtained. The drying oil monoglyceride may be derived from linseed oil or wood oil. Wood oil is heated with glycerol at 225°–258° C. in the presence of 0·05 per cent litharge. The glyceride obtained is heated with Congo or other acidic resins to yield a varnish.[14]

The Chemistry of the Running Process.—The nature of the changes which occur during the running of copals has been studied. Hellinckx states that the characteristics of the resultant products vary with the intensity of the heat supplied and on the rate of heating.[15] The products of decomposition include carbon dioxide, carbon monoxide, methane, hydrogen, hydrocarbons of the type CnHn, an oily distillate and an aqueous distillate. During the first stage of the running, i.e. up to 300° C., decarboxylation of dibasic carboxylic acids to monobasic acids occurs. Lactones are produced from hydroxy acids. Over the temperature range, 300°–350° C., a secondary decomposition occurs in which decarboxylation of the monobasic acids occurs with evolution of carbon dioxide. The lactones decompose simultaneously with evolution of carbon monoxide.[2] Higher monobasic acids may decompose into hydrocarbons and lower monobasic acids. Acids such as formic and acetic have been detected.[13] Hellinckx summarises the running process as melting, decarboxylation and cracking. Trost believes that decarboxylation occurs during the running of Brazilian copal.[16] Krumbhaar advises against excessive decomposition of the dicarboxylic acids since upon these acids many of the properties of the final varnish depend.[17]

Reduction of Acidity during Running.—It is obvious that decarboxylation explains the reduction in acidity which occurs during the running of copals. Some copals run to give products which are less acidic than others, e.g. Sierra Leone when run has a lower acidity than Congo. According to Hellinckx, when Congo copal is run until its acid value is

70 per cent of its original value the varnish obtained from it livers badly with zinc oxide. If, however, the acid value is reduced to 60 per cent of its original value the resultant varnish shows no livering tendency. It is believed that the livering is due to the presence of dicarboxylic acids and it is necessary to eliminate these to remove the reactivity.[18]

Dissolution of Copals in Oils by Other Methods.—By reason of the loss of resin incurred during the normal running process as well as the loss of valuable properties, much work has been accomplished on the incorporation of copals in drying oils in which the drastic treatment received during running is eliminated. Mertene describes how at 290°–300° C. under pressure in an autoclave, copals can be incorporated in oils without loss. The process is conducted in an atmosphere of nitrogen. The product has inferior drying properties.[3, 19] An alternative method is to heat the copal as a thin layer below 315° C. Pyrogenation occurs with a loss of only 8 per cent.[3]

Another method of incorporating resins which are normally insoluble in oil, with oil, is to add the finely powdered resin to an oil resin mixture at 260°–320° C. Damar or rosin is present in the oil-resin mixture. The acidity of the resultant mixture is reduced, if necessary, by interaction with lime or glycerol.[20]

Copals may be made oil soluble also by esterifying a hot solution of resin in organic acid with a polyhydric alcohol.[21] When a copal, phenol and an inert solvent are heated together oil and white spirit solubility are obtained.[22] The copal may be congo; the phenol, ordinary phenol or cresol, and the inert solvent, tetrahydronaphthalene. The products are clarified by treatment with fuller's earth. Terrisse heats copals at 275° C. and four atmospheres' pressure with naphthalene for two hours. The oil is added and the heating continued at 280° C. The naphthalene is removed finally by distillation.[23] A method due to Graham and Burrell involves the heating of copal with turpentine at 350° C. under pressure.[24]

Dissolution by Mastication.—Another process of inducing oil solubility in copals is by mastication and the process has been described in detail. Not only is the solubility increased by mastication but it is claimed that reactivity is increased also. If the temperature of mastication is high improved reactivity is obtained. If the temperature is low improvement in solubility occurs.[25]

The resin is masticated whilst plastic by passing over heated rollers. The temperature of mastication varies from 80°–205° C. and the duration of treatment from twenty to 120 minutes. Volatile products may be removed by the application of a vacuum. Two examples have been given. Congo is masticated at 150° C. for sixty minutes. Kauri is masticated with an equal amount of linseed oil at 121° C. for 120 minutes.[26] The kneading of resin to produce oil solubility may be carried out in the presence of solvent.[27] The mastication of resins on hot rollers may take place under pressure.[28]

Mastication of copals produces not only solubility in oil but solubility

in alcohol. This fact is important since it enables spirit varnishes to be produced from ordinary natural copals other than soft Manila copal. When copal resins are ground at 32°–50° C. under high pressure the resulting products are soluble in ethyl alcohol.[29] Manila copal milled at 132° C. for twenty to thirty minutes becomes soluble in hot butyl alcohol.[26] Manila, Pontianac, Benguela and Congo are made plastic by increased pressure, and masticated. Solutions of low viscosity are obtained with the products in ethyl alcohol, and may be used as shellac substitutes. A Congo copal soluble in ethyl alcohol is obtained by masticating it for two hours at a pressure of 90 lb. per square inch and 49° C. Frictional heat developed during the process is absorbed by water cooling.[30]

Cracking and Hydrogenation of Copals.—Mertens, Hellinckx and de Hoffmann have cracked Congo copal in the presence of hydrogen and a reduced nickel catalyst. Three types of oily hydrocarbons were obtained, terpenes, hydrocarbons richer in hydrogen than terpenes, and hydrocarbons poorer in hydrogen than terpenes. The most important factor which influences the reaction is temperature.[31]

In a previous paper the same investigators describe the hydrogenation of Congo copal at 350°–400° C. and 100 kg. per sq. cm. pressure using nickel quartz as catalyst. Among the products obtained were carbon dioxide, carbon monoxide, methane, products of the types C_nH_{2n}, and C_nH_{2n-2}, and liquid products boiling below 200° C. The mechanism of the reaction is given as reduction of double bonds and decomposition of carboxyl groups.[32]

Modifications.—Congo and other copals may be modified by interaction with other compounds. The most important modification is esterification with glycerol to yield copal esters. The resins are dealt with at length elsewhere.

Other modifying agents for run copals are lime, magnesia and litharge. Very hard resins of high melting-point are obtained from masticated copals and phenol formaldehyde products. Masticated copals are claimed to react readily with metallic oxides, hydroxides and salts; with monohydric, polyhydric and phenolic alcohols; with hydroxy compounds like mono and diglycerides, with amines, and with oxygen, sulphur and halogens.[26] Natural copals have been acetylated to yield products described by the name "acetocopals." They are stated to be valuable raw materials and have good solubility.[2, 15]

Testing

It is necessary, in the varnish laboratory, to examine natural copals with reference to their suitability for varnish manufacture. The following routine procedure has proved useful. Where many grades of various copals are used, standard samples of each are kept. These samples should be representative, and of about two pounds' weight. Bulk samples of the copals under consideration are compared with standard samples for colour, homogeneity, size, extent of fossilisation and

quantity of extraneous matter. Self colours of the copals can be quite easily compared. Some grades of copal are deliberate mixtures of pale and dark resin and this can be recognised readily. After this preliminary examination, samples are selected and a hundredweight or so of each ordered. These are then run under normal practical conditions to produce a varnish, and this varnish is compared for colour, dry, amount of thinners necessary to yield normal varnish viscosity and for other properties, against the same varnish made from standard copal. Running losses are also determined by weighing carefully all the constituents of the varnish and the final yield. Because of the loss of volatile thinners during thinning it is preferable to compute running losses on the copal-oil basis. The amount of thinners required to obtain a varnish of standard viscosity is a good indication of the standard of copal used.

The thinners used may be determined by direct weighing or by a percentage volatile determination.

Properties

Age and Solubility.—The older a copal is the less its solubility. This according to Nagel and Kornchen is attributed to the formation of compounds of higher molecular weight or of compounds which are chemically indifferent.[33] The same workers have evolved a method whereby the solubility of copals in alkaline solution is taken as the criterion for distinguishing different types of copal. A clear solution was obtained with Manila copal in 1·5 per cent potassium hydroxide. Other copals such as Kauri, Zanzibar and Congo gave substantial amounts of insoluble matter, i.e. from 48–64 per cent insoluble. Differences of solubility in methyl alcohol were observed also. Using a large excess of alcohol, Kauri and Manila copal were 60 per cent insoluble. Zanzibar gave substantially more insoluble matter. The solubility of Congo is intermediate between that of Manila and Zanzibar. Congo undergoes substantial esterification with methyl alcohol.

Smell.—Experienced workers can differentiate between copals by mere physical examination. The smells of copals, freshly fractured or gently warmed, are often characteristic. It is possible, by means of smell, to distinguish copals like Manila, Kauri and Congo.

Liebermann-Storch Test.—The Liebermann-Storch test for copals in varnishes is unreliable or of little value. Most copals merely give a brownish coloration which is inconclusive. Rosin in the presence of copals can be detected normally by this test, but Stock has reported that the test gives both positive and negative results for genuine copals.[34] Hellinckx states that the fluorescence of Congo copal in ultra-violet light is characteristic.[15]

Uses

Congo copal is still used extensively in the varnish trade. As indicated already it is the basic resin for the manufacture of hard gloss paints and

enamels. It is still a favourite also for the old well-established type of decorators' varnish.

For durability it is easily surpassed by synthetic varnishes of the alkyd or phenol formaldehyde type. Allen and Sprinkel, however, make out one point in favour of copal varnishes for exterior use. They point out that when a film derived from natural resin weathers, it does so with the formation of fine cracks and requires very little preparation before revarnishing. Modified phenolics give much larger cracks and a greater expenditure of energy is necessary for preparation.[35]

For hard drying interior varnishes Congo copal will hold pride of place for many years to come.

Other uses for copals are in the production of gold-sizes although they have been displaced to a large extent by tung oil-rosin blends. With lack of tung oil, however, there has been a tendency to revert to the copal type of gold-size again. For the production of varnishes for printed tin they hold an extremely important position. Using first grade Congo with all the necessary precautions in manufacture it is possible to produce excellent silver stoving varnishes. Copals also form the basis of many gold stoving varnishes. Due to the fact that run copals are not completely soluble at all dilutions, they sometimes form the basis of solvent resisting varnishes or enamels. The harder types of copal yield, with but little oil, the hard rubbing furniture varnish. Such varnishes are cheap and give good results although they are inferior in most respects to similar products based on a hard phenolic resin.

Kauri Copal

After Congo the other natural copals are used to a considerably diminished degree. The only other copals which are used to any real extent at all are Kauri, Manila, Sierra Leone and Benguela. Kauri was a very popular resin but it is fast losing its popularity. This may be due to its relative scarcity and its extremely high price. The Kauri of commerce is a fossil resin derived from the New Zealand Kauri pine (*Dammara Australis*). Kauri is sometimes described as New Zealand dammar.[36] Heaton lists the following grades of Kauri: dial, range, swamp, chalk, rubbling and chip.[37] Although the scarcity of Kauri was a generally accepted fact, Hosking reported a few years ago that there is still as much Kauri in the ground as that obtained so far from it.[38] Kauri can be obtained by incision. This is known as bush Kauri. Kauri has been obtained also by extraction of Kauri timber with alcohol. The product is purified by heating with a mixed solvent comprising ethyl acetate and benzene.[39] Hosking has described a solvent process for the production of good quality Kauri from a crude starting material, in which the crude Kauri is dissolved in a mixed solvent comprising benzene (7 parts) and acetone (3 parts) at 50° C. The impurities are removed by settling.[38] A similar process is described whereby crude Kauri is dissolved by warming in acetone or in a mixture of acetone and benzene.

The impurities are removed by filtration, the solvent removed by steam distillation and the resultant product dried under vacuum to yield a hard resin.[40] Flotation methods are also used in the purification of Kauri. The mild alkali treatment of a Kauri solution is claimed to produce decolorisation. The coloured components are removed as a separate dark layer.[41] Kauri is very easy to run.

The chief uses of Kauri nowadays are in special media for coach painters, in gold-sizes and in hard rubbing furniture varnishes.

Manila Copals

Manila copals include the following types: Pontianac (Borneo), Macassar, Sambas, Java, Lowoe, Ternate and Labuan.

Pontianac may be obtained as a fossil resin or by incision. It has the smell of turpentine. It is a hard resin and the fossil type is used in the manufacture of oil varnishes. Macassar copal is not generally considered to be such a good grade as Pontianac. Sambas copal has been examined by Stock.[42] It is obtained from Pilau copal by sorting.[43] Java copal is a hard type. Ternate is soft and is appreciably soluble in alcohol. Stock describes a copal from the Fiji Islands which he assigns to the Manila group. It dissolves in alcohol or turpentine and yields films with good gloss.[44]

Mantell and Rubenkoenig believe that Manila copal consists chiefly of four different resin acids. Manila copal may be used as a shellac substitute by the addition, either of nitrocellulose, or of beeswax and fatty acids.[45]

Hard Manila copals are sometimes used in decorative varnishes although their durability is not particularly good. They are used, however, in gold stoving lacquers in which the gold colour of the film is obtained by carbonisation at the high temperatures used. The shade of colour produced from Manila copal films on high temperature stoving is quite pleasing.

The most important use for Manila copals is in the manufacture of spirit varnishes. It is only the softer varieties of resin which are alcohol soluble. As the hardness of the resin increases the viscosity of the alcoholic solution increases simultaneously. When the copal is very hard the tendency to alcohol insolubility becomes most apparent. Spirit soluble Manilas contain substantial amounts of dirt, wood, bark, twigs and other extraneous matter, and this must be remembered in assessing the value of a consignment of copal to the consumer, and in formulation. Soft Manila copal is dissolved in alcohol by cold churning, the insoluble matter removed by rough straining, and the solution passed through either a centrifuge or a filter press. Absolute clarity may not be obtained in either case but this is not normally considered to be a serious defect. The molecular weight of the alcohol used to effect solution of Manila influences the viscosity of the final solution. The higher the molecular weight the greater the viscosity.[46]

The hardness, and water resistance of Manila spirit varnishes can be improved by the incorporation of ethyl cellulose. Up to 25 per cent, calculated on the weight of the Manila copal, is recommended.[74]

Sierra Leone Copal

Fossil types are known by the names Kissel copal and Pebble copal, but the bulk of the present supply is obtained by incision of the *Copaifera Guibourtiana*. Good grades are very pale and can be run to yield very pale varnishes. Pale Sierra Leone copals are still used in the production of media for white hard gloss paints and enamels.

Benguela Copal

This is sometimes known as Lisbon copal and is obtained from West Africa. It is a fairly hard resin and is claimed by some to have outstanding durability for a natural copal. The author was not able to confirm for this copal any great superiority in this respect over other copals.

Other Copals

There are many other copals in existence, although from the varnish maker's point of view they are unimportant. They are included here, with brief notes, only for the sake of completeness.

Zanzibar is a hard fossil resin from East Africa. It sometimes occurs under the name Animi, and because of the similarity of its rough surface to goose skin it may be referred to as goose skin animi. Other East African copals are Mozambique or Inhambone, Madagascar and Lindi. Apart from Congo and Benguela other West African copals are red and white Angolas, Accra, Benin, Gaboon, Loango and Cameroon.

South American copals have attracted some attention, and Brazilian, Columbian, Demerara, Locust and Para are known. Demerara copal is obtained from British Guiana. Stock has described the properties of two copals from this source. Both the fresh and the fossilised types are stated to be satisfactory varnish resins.[47]

Demerara copal has to be run to a high temperature to induce solubility in oil. Vigorous frothing occurs and the introduction of carbon dioxide is suggested to control this. Varnishes based on this copal dry with hard glossy films. Esters may be made from this copal to permit its use with basic pigments.[48]

Other newer resins from South America have been investigated recently. Soft Jatoba or Trapoca resin of Brazilian origin is exuded either from the roots of trees or from the twigs and branches. The resin from the roots is harder than that from the branches. It is said to be soluble in turpentine without further treatment, in contrast with hard Jatoba resin which needs running.

Kemner reports that Brazilian Jatoba copal does not yield such hard films as Congo and takes longer to dry.[49]

Jatoba resins have similar properties to damar, except for their substantially higher acidity. Soft Jatoba resin is suggested for use in spirit varnishes. Durability of these resins is not good and they should be used for interior varnishes only. Their acidity can be reduced by esterification with glycerol, and this makes possible their use with basic pigments. Like damar, if the wax is removed from the resins by solvent treatment they may be used with nitrocellulose.[50]

Another Brazilian resin is Jutahycica which is a fossilised variety.[51] It is exuded from the roots of Jutahyassu and Jutahy trees.[52] This resin can be run to yield oil varnishes, with properties similar to those obtained with Kauri.[53] Wramba copal, also a native of South America, is a good resin for oil varnishes, drying well to hard films with good gloss.[49]

It is now reported that copals, suitable for conversion into dark varnishes, have been found in the Caucasus and in the far Eastern U.S.S.R.

Amber

Source.—Although amber is rarely used in varnish manufacture, its availability and the attention it has attracted in recent years earn for it a place in any modern treatise on varnish manufacture. Amber is a fossil resin found chiefly in the blue earth of East Prussia. It is an exudation of *pinus succinifera*. The blue earth is at the bed of the ocean. Amber may be found also in glacial deposits or it may be washed up on beaches. Schmid gives the ratio of blue earth to amber as 10,000 : 1. The reserve of amber is computed at 5,000,000 tons.[54] The properties of amber from different sources vary considerably.

Production.—The crude amber with its earthy impurities is washed with water under pressure and sorted by hand. Amber is a yellow resin and is available in three forms : rough amber, pressed amber and melted amber.

Pressed amber is obtained by amalgamating small pieces under pressure. Melted amber according to Schmid is the grade most useful for lacquers. Rough amber is used for ornaments, jewellery, etc.

Effect of Heating.—When amber is heated at 320°–360° C. oil of amber and succinic acid are distilled off. Melted amber is the non-volatile residue. If amber is subjected to further dry distillation, aliphatic acids including acetic, butyric, valerianic, caproic and succinic acids are split off, in addition to water and hydrocarbons. Hydroxy acids have been detected by Plonait during degradation of amber.[55]

Composition.—The chemical examination of amber has been conducted by Schmid and Hosse.[56]

Schmid and Erdös have examined amber also by solvent extraction followed by hydrolysis. The presence of succinic acid was confirmed. Abietyl compounds and borneol were detected also. Resinous components after dehydrogenation yielded polymethylnaphthalenes and -phenanthrenes.[57] Dehydrogenation of the alcohol insoluble portion with selenium yielded 1 : 2 : 5-trimethyl-naphthalene.[58]

Properties and Uses

Amber is claimed to be the hardest known resin.

The resin is generally insoluble in most solvents, but after melting its solubility improves. It becomes soluble in turpentine, benzene, carbon disulphide, chloroform, ether, and hot linseed oil. The extent of the solubility in petroleum hydrocarbons appears to be controversial. The melted resin is insoluble in alcohol and acetone. The resin is soluble in butyl alcohol containing hydrochloric acid if the mixture is refluxed.[54] Treatment of the resin with ammonia followed by caustic soda, enables solutions to be obtained in a mixed alcohol-carbon tetrachloride solvent.[59]

An amber soluble in polymerised and unpolymerised drying oils and in solvents, is made by heating by means of a liquid medium which avoids excessive temperature during the process.[60] Amber may be incorporated in vegetable oils by grinding the mixtures in colloid mills.[61]

The use of amber in linseed oil varnishes is mentioned by Hess who comments very favourably on their value as corrosion resistant stoving finishes for light metals and their alloys. The higher the temperature of stoving and the greater the duration, the better the corrosion resistance of the resultant film.[62]

Other outstanding properties of amber varnishes are that they have excellent resistance to moisture and to heat.

Kemner states that compositions from amber are matched only by nitrocellulose in respect of hardness, gloss and elasticity.[60]

Stock claims that amber esterifies easily. The glyceryl ester of amber with oiticica oil gives pale hard varnishes.[63]

Damar

Source and Grades.—Damar is not used in large quantities in the modern varnish factory. In fact, it is used almost exclusively in two types of material only, in crystal paper varnishes, and in nitrocellulose lacquers after "dewaxing." Damar is an exudation and is obtained from the East Indies, Malaya and Siam. It comes on the market in the form of yellow lumps or granules. Seed damar is a fine variety containing resin dust.

Many different types of damar are produced. Batavian damar is generally considered to be a first grade resin. It originates from Sumatra, Borneo and Java. Pedang (or Padang) damar comes from Sumatra. Singapore damar is not such a good grade as Batavian and consists of a mixture of damars from various sources. Pontianac damar and Borneo damar both originate from Borneo. The latter grade is smaller and dirtier than the former. Hiroe damar is also of Borneo origin and is a fossil type. Yellow Siam damar is a very pale grade. Black damars are also available, and these include Batu damar and black East India damar. Both originate in Malaya. The resins are dark coloured and are mixtures. Barry gives Hitam as the best grade of black damar with Senggi as a softer grade. Stock has described a black damar from Sumatra.

Mata Kuching damar was found to consist of pale and dark resin. The pale grade is stated to be satisfactory for varnishes. Gardner and Sward have examined a Brazilian damar and report that it is less soluble, paler and harder than Singapore damar.[64]

Manila copal is sometimes called white damar.

Composition.—Damar consists chiefly of a mixture of two resenes, α-damar resene and β-damar resene. In addition, damarolic acid is present.[65] The resenes constitute about 60 per cent of the resin.

Solubility.—Damar is soluble in aromatic hydrocarbons, aliphatic hydrocarbons, turpentine, ethyl acetate and esters generally, chloroform and carbon disulphide. It is insoluble or only partly soluble in alcohols, acetone and aniline. Damar does not always give clear solutions in solvents, and in white spirit especially the solutions may be distinctly turbid. Solutions in aromatic hydrocarbons or turpentine do not usually exhibit such pronounced turbidity, and it is frequently possible to clarify a turbid white spirit solution by addition of either of these two solvents. Mantell and Skett have indicated the wide variation in viscosity which is obtained by dissolving damar in various petroleum solvents.[66] Resins which are not very soluble in benzine alone, are soluble in a mixture of benzine and a solvent containing a hydroxyl group, or in a mixture of benzine with a solvent containing a carboxyl group. Thus solvents for damar comprise a mixture of benzine (90 parts) and ethyl alcohol (10 parts) or a mixture of benzine (95 parts) and diacetone alcohol (5 parts).[67]

Purification.—Damars may be purified by solvent extraction. The following is a method of treatment. The damar is dissolved in a mixture of chlorinated hydrocarbon and alcohol. The insoluble material is removed by filtration and the filtrate evaporated to regenerate the resin.[68]

Dewaxing.—One of the chief uses of damar is with nitrocellulose, but damar contains constituents described as "wax" which are not completely compatible with nitrocellulose. These are removed by solvent treatment. Dewaxing is accomplished by dissolving the damar in a good solvent and precipitating the wax by means of a non-solvent for it. Thus damar is dissolved initially in ethyl acetate or aromatic hydrocarbons and methyl alcohol is added to precipitate the wax. The clear filtrate is evaporated if desired to yield the dewaxed damar.

Testing.—Damar is usually tested for suitability for use in varnish manufacture by conducting a few very simple routine tests on it. It is usual to test for solubility, amount of dirt and colour. These properties can be examined simultaneously. About 40 grams of damar are dissolved by churning in 60 grams of solvent which may be white spirit, turpentine, or naphtha or blends of these. The solutions are allowed to stand and the supernatant liquid decanted off. This may be compared with the solution obtained from a standard grade for colour, turbidity and viscosity. If the solution of the resin under test contains

not more than the amount of soluble matter in solution which is present in the standard solution, but has a higher viscosity, then the damar under test has inferior solubility. The material insoluble in the solvent after decanting the supernatant liquid can be washed with solvent and weighed. The percentage insoluble can be compared with that in the standard damar and calculations made for price comparisons.

Properties

Damar has an acid value of the order of 30–35. It is a soft resin but powders with rubbing. It exhibits strong solvent retention as evidenced by the tackiness of its films. The tackiness is more apparent in short oil films than in the longer oil variety. Damar possesses a characteristic odour especially when warmed. Its durability is not good and hence it is used chiefly for interior decoration. The resin has good gloss. It is fairly resistant to chemicals due to the presence of resenes. Damar does not yellow appreciably. Methyl cyclohexyl stearate has been suggested as a suitable plasticiser.

Uses

The uses of damar may be enumerated as follows. It is used for pale crystal paper varnishes, varnishes for maps, etc., varnishes for toys, media for toy enamels, nitrocellulose lacquers to improve the gloss and adhesion, overprinting varnishes and alkyd resins.

In nitrocellulose lacquers damar has been compared with alkyds, modified phenolics and ester gum, and conclusions reached are that damar compares favourably with these resins for hardness, durability, water resistance and clarity of film.[69] Mantell and Rubenkoenig, claim that except for alkyds, damar is superior to other resins for use in lacquers.[70]

Other workers have compared damar with other resins in nitrocellulose lacquers. The resins compared were run Congo, dewaxed damar, pure phenolic resin and maleic anhydride resin. The results may be summarised as follows : Damar showed inferior alcohol resistance. Resistance to caustic soda was best with pure phenolic resin, followed by damar, Congo and maleic resin. Pure phenolic and damar were resistant to boiling water. Congo, damar and pure phenolic all resisted salt solutions, and all resins resisted the action of petrol.[71]

Many claims have been made concerning the suitability of damars for incorporation in alkyds. Kemner mentions them as bodying agents for alkyds.[72] The effect of Batavian and "Run" Black East India damar on alkyds has been examined by Mantell, Skett, Holzberger and Allan. The latter yields darker and softer films but the former yields alkyds with good hardness and gloss which are pale in colour.[71]

A modification of damar is recorded in which an alcohol is obtained from damar by reduction. This damar resin alcohol, when dissolved in a solvent comprising turpentine (40 parts), and alcohol (10 parts), is used as a varnish for pictures.[73]

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Rosin (Colophony)

Rosin is used in considerable quantities in varnish manufacture. Many consumers of varnishes regard the presence of rosin in a varnish as an indication of inferiority. This assessment of rosin is only partly true, for whereas it forms the basis of many cheap finishes, it possesses certain valuable properties which are exploited with advantage in a variety of excellent finishes.

Source.—Rosin is contained in the exudation of the Pinus species which includes: *P. palustris*, *P. maritima*, *P. pinaster*, *P. australis*, *P. laricis*, and *P. taeda*. The first mentioned is the source of American rosin, and the second provides the French grade of rosin. Resins from *P. insularis*, *P. caribaea*, *P. insignis*, *P. pithyusa* and *P. sylvestris* have been examined.[1]

Apart from America and France, rosin is obtained from Spain, Portugal, Greece, China and Mexico.

Production of Gum Rosin and Wood Rosin

Gum rosin.—Broadly speaking the varnish maker uses two different types of rosin, namely, gum rosin and wood rosin. Whilst the former variety is perhaps the more popular in the United Kingdom, the consumption of wood rosin in the United States exceeds that of the gum rosin. Gum rosin is an exudation product of the living tree obtained from the oleoresin. Wood rosin is obtained by more drastic treatment from dead stumps. Since the production of these two types of rosin is different they are dealt with under separate heads.

Oleoresin is obtained by making an incision in the tree when the oleoresin runs out and is collected.

Collection of the Oleoresin.—The oleoresin is collected in open cups which are emptied from time to time. It may be contaminated with wood chips, bark, leaves, dust, insects and rain water. The use of covered cups has been suggested to prevent contamination by dirt, etc., and to prevent, simultaneously, excessive evaporation of volatile

constituents.[2] When the oleoresin first exudes it is a clear viscous solution of rosin in turpentine, the turpentine being almost pure pinene. Due to subsequent crystallisation and loss of volatile constituents the product collected becomes opaque and very viscous. Smith [3] estimates that as much as 8 per cent of water may be present also. About 75 per cent of the oleoresin is rosin. This is obtained by subjecting the oleoresin to distillation.

Treatment of the Oleoresin. Removal of Impurities.—It is not possible to remove all the extraneous matter from the oleoresin before distillation but the lighter material, such as bark, wood chips, etc., which floats on the surface of the molten rosin, is sometimes removed by skimming. This necessitates an interruption of the distillation process. The undistilled residue constitutes rosin, and the distillate is turpentine. Distillation may be conducted with the assistance of steam or vacuum. The molten rosin in the still may be cleansed further by straining or filtering. High temperatures are necessary for these processes and may vary around 150° C. If the molten rosin is strained it may be passed through a series of sieves and finally through cotton batting. Other methods of cleansing rosin from dirt consist in dissolving the rosin in a solvent, filtering the solution and distilling off the solvent. Protected methods involve the separation of dirt by settlement. The density of the rosin is reduced by heating, or the rosin is dissolved in turpentine or other solvent. The heavy dirt settles out. Separation of water may be effected also by settlement from a turpentine solution, and this process may be facilitated by adding water-soluble salts to increase the density of the aqueous solution. Rosin may be cleansed by distillation under reduced pressure.[4] This is not, however, a commercial proposition for mere removal of physical impurities, although vacuum distillation is used in Great Britain for the removal of chemical impurities, which have a harmful effect on electrical properties. Smith has examined the question of dirt in commercial rosin. He reported that most grades had fine particles of dirt in suspension, in amount not usually exceeding 0·1 per cent.[3] He has shown also that the presence of water in rosin has a strong contributory effect in causing the appearance of suspended dirt, and emphasises that to obtain clean rosin it is essential to remove the water, either before filtration or immediately after.

The following method was devised for the separation of water from rosin. A 30 per cent solution of rosin is made in turpentine and the temperature raised to 95° C. The water is removed by separation or decantation and the turpentine solution filtered through filter paper. After filtration 3–4 per cent of water remains in suspension and this is removed by washing with further lots of water at 95° C. Good clean gum rosin results.

Artificial Stimulation of Exudation.—The yield of resinous exudation may be increased by the application of an irritant to the incision. Irritants used include 20 per cent aqueous ammonia, a 50 per cent

solution of sulphuric acid or a 6 per cent solution of formic acid. A thinner exudation is obtained if an irritant is used.[5] A more recent method of stimulation consists in removing portions of the bark and spraying the exposed areas with sulphuric acid (80-100 per cent). Hessenland has given a comprehensive list of acids, alkalies and salts which may be used as stimulants.[64] Loycke does not consider the presence of irritants in the oleoresin to be harmful usually, although they may affect subsequent esterification. Further, the presence of mineral acid tends to promote the conversion of the resin acids to abietic acid. Its effect, however, is nullified by heating at 210° C. for fifteen minutes.[6]

Production of Rosin by Solvent Extraction.—Rosin may also be extracted from raw wood by solvent extraction. Solvents used are solvent naphtha,[7] and aliphatic water miscible solvents. A protected method involving the use of a water miscible solvent consists in extracting the wood with this solvent. A low boiling petroleum hydrocarbon is added which is a solvent for the rosin but which is immiscible with the original extraction solvent. The rosin is obtained by separating the hydrocarbon solution and evaporating the solvent.

Wood Rosin

The great pine forests of America—a belt of some thousand miles long and two hundred miles wide—situated along the seaboard of the South and South-Eastern States, began to shrink critically. In the place of the majestic trees vast numbers of protruding stumps were left. It is from these dead and weathered stumps, either blown out of the ground by explosives or wrenched out by special tractors, that vast amounts of wood rosin are produced to-day.

The weathering occupies at least ten years, and during this time the composition of the original oleoresin alters substantially. Whereas, originally it was a solution of rosin in turpentine, weathering produces considerable changes. The pinene is converted in part, to other cyclic hydrocarbons and alcohols, and the rosin-turpentine ratio alters from 3 : 1 to 6 : 1.[63]

Weathering of the stumps is essential to remove the useless outer sap wood, and to expose the valuable heartwood. The portion of the stump which is used, is that extending to about two feet below the ground —the tap-roots are cut off and discarded. The prepared stumps are then shredded into thin short splinters.

Garvie (*loc. cit.*) states that the turpentine and rosin are obtained from the wood by two processes, but the second mentioned is the more popular.

1. Volatile constituents are first removed by saturated or superheated steam, and the residue is then extracted with solvent to remove the rosin.

2. Alternatively, the wood is immediately extracted with a suitable solvent, and the resultant solution is fractionated by distillation.

Varnish Constituents

The resultant rosin solution is treated to remove soluble oxidised compounds, filtered to remove extraneous matter, and then evaporated under reduced pressure. Wood rosin, FF grade, is obtained.

Refinement of Rosin. Colour

The production of pale rosins has been the subject of much investigation. This is especially true of the wood rosins which are naturally a dark ruby-red colour, and probably most of the attention has been devoted to these rosins rather than to the gum rosins.

In short, the improvement of colour of rosin is effected by two methods, namely, treatment with activated earths or by selective solvents. The former method has been described by Garvie, and it consists in first washing the rosin solution (20 per cent concentration) with water to coagulate colloidal matter and then in passing it through vertical towers packed with earth. The mechanism of the decoloration involves, first a preferential absorption of rosin by the earth, and subsequently an absorption of colouring matter by the rosin-saturated earth, and an elimination of the previously absorbed rosin. The resultant pale solution is distilled under vacuum to yield a pale rosin.

About a quarter of the original weight of rosin is retained by the earth, but this is substantially reclaimed by a mixed solvent treatment.

Many methods for rosin refinement or decolorisation involving solvent treatment have been patented, and whilst some of them are applicable to large-scale production, others have never been developed from the research laboratory stage. The methods used may be sub-divided into the following groups :—

(*a*) Treatment with solvent only.
(*b*) Treatment of rosin solution with a chemical reagent.
(*c*) Chemical treatment of rosin followed by solvent extraction.

Solvent Treatment

Rosin is dissolved in a low boiling petroleum hydrocarbon, and the solution diluted to give a rosin concentration of 7–10 per cent. Some precipitation occurs. The precipitate is removed and furfural added. This results in the separation of two layers. A pale rosin is obtained from the top layer after removal of petroleum hydrocarbons, by distillation.[9] The presence of water in the furfural is claimed to be advantageous. A similar method consists in dissolving the rosin in a petroleum hydrocarbon containing furfural, and the insoluble reaction products are separated.[18]

A gaseous hydrocarbon, which by adjustment of temperature and pressure can be liquefied, is used as a rosin solvent. Coloured compounds are removed by extraction with an immiscible solvent.[13]

The impurities in rosin may be dissolved out of a solution of it by means of a nitroparaffin, the nitroparaffin being immiscible with the

rosin solution. The rosin solvent and the nitroparaffin are used in the ratio of 25 : 20 by volume. The nitroparaffins may be replaced by nitroalcohols.[20] Rosin may be purified by extraction with methyl alcohol or an alcoholic solution of resorcinol.[21]

The solvent treatment sometimes simply consists in dissolving the rosin in a suitable solvent, separating the insoluble matter and reclaiming the rosin by evaporating the solvent. A low boiling petroleum hydrocarbon, rich in hexane, with an aniline point above 60°, used in amount up to ten times the weight of rosin, has been suggested as a satisfactory solvent.[65]

Treatment of Rosin Solution with a Chemical Reagent

A solution of rosin is treated with a solution of oxalic acid in a non-aqueous solvent which is immiscible with the rosin solvent. The coloured compounds of the rosin are thus removed.[10, 69] An organic solvent which is immiscible with the rosin solvent is used as a vehicle for introducing sulphur dioxide which effects the removal of coloured compounds.[11] A hydrocarbon solution of rosin is washed with an hydroxyalkylamine. Alkylamine oxyabietate is precipitated and the rosin is obtained from the clear solution by evaporation.[15] Rosin is refined by treating it with a halogen at 150°–350° C.[16] A solution of rosin in hydrocarbon is treated with an aqueous solution of silicofluoride. After removal of the silicofluoride solution the rosin solution is treated with an immiscible solvent for extraction of coloured substances.[17] An organic thiocyanate immiscible with the rosin solvent is added to a rosin solution. After the reaction the rosin solution is separated.[19] A purified rosin is obtained from crude pine resin by extraction with paraffin oil. The extract is treated with caustic soda and the solution of alkali salts when separated can be treated with acid to regenerate the rosin.[23]

Chemical Treatment of Rosin followed by Solvent Extraction

When rosin is heated with a boron compound at 100°–225° C. a reaction occurs between the boron compounds and the colour bodies of the rosin. Since this reaction product is insoluble in rosin solvents, the refined rosin can be obtained by extraction.[12]

Other Methods of Refining

There are other methods of refining rosin which are difficult to place under any one particular heading, and for convenience only they are grouped together.

Rosin may be bleached by the action of sunlight or ultra-violet light but obviously the method presents difficulties on the commercial scale.

Another method of purification consists in treatment with phenol or furfural, followed by vacuum distillation.[22]

Or the colour can be improved by melting the rosin and allowing the impurities to settle for from half to one hour. The clear melt is decanted into a second vessel and boiled for one hour with sodium chloride solution. The boiling is continued with successive lots of salt solution until a pale rosin is provided.[14]

Blowing of rosin at elevated temperature (250°–350° C.) with carbon dioxide, nitrogen or steam, results in the removal of volatile constituents and has the dual effect of reducing odour and colour.[68]

Composition

According to Smith [3] rosin consists of approximately nine parts of isomeric acids with one part of neutral or unsaponifiable matter. Small amounts of impurities may be present also. The principal constituent of rosin is abietic acid or its isomers. Some investigators have attributed the difference in behaviour of rosins to the existence in them of different acids. Thus Kemner states that the chief acid constituent of most European rosins is pimaric acid in contrast to other rosins containing abietic acid.[24]

Tochirch separates rosins into two groups depending upon whether they contain pimaric or abietic acid. American rosin contains abietic acid and French rosin pimaric acid.[25] Resin from the Alpine fir contains abietic and probably pimaric acid as well.[26]

From Swedish pine oil, Aschan has obtained an isomer of abietic acid, pinabietic acid,[27] and from American and Finnish rosins he has obtained a number of colophenic acids.[28] Fahrion believes these acids are oxyabietic acids.[29] American rosin, according to Stock contains α, β and γ abietic acids.[30] Other acids said to be present in rosin include sylvic, α, β and γ pinic acids,[31] and sapinic acid. Mixtures of sapinic acids were obtained from Scandinavian pines.[32] Vocke reports the presence in American pine rosin of sapic acid. It deposits from freshly prepared resin on standing.[33] Dieterich records the presence of some pyrocatechuic acid.[34] Matlack and Palkin have found among the neutral compounds of rosin, resenes, hydrocarbons and esters. These components may be separated from the acids by neutralising the acids with alkali and extracting the soaps, thus formed, with ether.[35] The composition of pine resin undergoes changes on ageing or heating.[36]

The Chemistry of Abietic Acid.—Considerable investigation work has been conducted on the chemistry and constitution of abietic acid and allied compounds. Fahrion, Easterfield and Bagley, Virtanen, Kolbe, Grün, Köhler, Levy, Dupont, Stock,[30] Aschan,[27, 28] Soane,[37] Paul,[31] Cohn,[38] Knecht and Hibbert, Klason and Köhler,[32] Ruzicka, Arbusov, Kraft, Arbuzov and Schapschinskaja, Palkin and Harris, Fieser and Campbell, Bevan, Fleck and Palkin, Sternbach and Lombard,[39] have all contributed to these aspects of the subject.

Properties

Physical and Chemical.—Rosin is a brittle resin which powders easily between the fingers. It becomes sticky readily when warmed.

From the point of view of electrical insulation, gum rosin is superior to wood rosin, at least in the presence of mineral oils, although there is little to choose between the two types of rosin in solid form.

Colour.—The colour varies considerably from very pale yellow to a dark reddish-brown and even black. Standards issued by the Department of Agriculture, U.S.A., are designated by letters. Thus the darkest grades occur in the range from A to F, with the palest grades from N to X. A good series for adoption as colour standards would include samples of D, E, F, G, H, I, K, M, N, WG, WW and X. D grade is almost black. FF grade is specially reserved for wood rosin. WW is sometimes described as water white although this description is not strictly true. WG is described as window glass grade. Sometimes rosin is sold under the designation EP. The French system of grading is by including the letter A in the description. Thus the greater the number of A's used the paler the grades.

Melting-point, Acidity, Solubility.—The melting-point of rosin is about 60° C. by the capillary method, but in exceptional circumstances, if it is in a highly crystalline condition, much higher figures are obtained. It has an acid value of 168–172. Wood rosin, grade FF, sometimes has a lower melting-point and acid value than American gum rosin. Rosin is readily soluble in most organic solvents, including aliphatic and aromatic hydrocarbons, turpentine, ketones, chlorinated hydrocarbons, carbon disulphide, alcohol, esters, and drying oils, both unpolymerised and polymerised. It has, moreover, outstanding compatibility with most other varnish constituents. Rosin reacts with maleic anhydride to yield valuable resins, an aspect which is discussed in greater detail elsewhere.

Atmospheric Oxidation.—Rosin undoubtedly deteriorates on exposure to air, especially if the rosin is in a finely divided form. Samples of rosin powder have been examined by the Author and have shown a substantial amount of matter insoluble in white spirit and oils. Fahrion believes that the deterioration of rosin on exposure to air is due to the formation of unstable peroxide acids which are insoluble in petroleum hydrocarbons.[40]

The Reactions between Rosin and Maleic Anhydride, Metallic Oxides or Glycerol.—The reaction between abietic acid and maleic anhydride has been studied, by Ruzicka,[41] Arbusov and others. Arbusov has reported the difference in reactivity of rosin acids with maleic anhydride. Many rosin acids react readily to yield addition products, but the acids from French rosin do not undergo this reaction.

Being acidic, rosin reacts readily with basic and other oxides to yield metallic soaps. Metallic soaps are dealt with at length in the chapter

devoted to their consideration. Its high acidity causes feeding with basic pigments. Rosin ester is another valuable reaction product.

Liebermann-Storch Reaction.—Rosin gives positive results for the Liebermann-Storch and Halphen-Hicks tests even if it is present in small amounts only, or in the combined form as in ester gum, rosin modified phenolic resins, and resinates, etc. Alkyds sometimes interfere with these tests.

Peptising Action. Reclamation of Gels.—Rosin is a very good solvent and may be used as a stabiliser for varnish compositions of uncertain stability, and as a flux during the melting of certain resins and other substances. It has a strong peptising action on partly gelled oils and is especially effective in regenerating highly bodied tung oil. All that is necessary is that the rosin is added rapidly to the hot melt in the form of small pieces and stirred vigorously. If the operation is successful the highly bodied mass will be broken down in a few minutes. Similarly, it may be used with tung oil during its heat treatment. The time for gelation is lengthened considerably and varnishes are obtained which permit the addition of very large amounts of thinners.

Effect on Dry.—Varnishes made from rosin do not dry very well in that they have a tendency to possess residual tack, unless they are formulated with large amounts of tung oil.

Crystallisation.—A defect of rosin which is often disturbing is its tendency to crystallise from solution. The tendency to crystallise may occur with alcoholic or white spirit solutions, although it is more common with alcohol. The common practice of producing spirit varnishes based on Manila-rosin mixtures often demonstrates the phenomenon. It is necessary to keep the concentration of rosin within limits if trouble is to be avoided, although the presence of Manila resin does appear to help in maintaining the rosin in solution. The tendency to crystallise is believed to be due to the presence, in the rosin, of acidic isomers of indifferent solubility. Albertson has examined the crystallisation of rosin.[42] Methods of preventing crystallisation have been suggested. A rosin with no crystallising tendency is made by allowing the original oleoresin from the tree to crystallise completely. The crystals are removed by filtration and the rosin obtained by evaporation of volatile material.[43] Heating of rosin at elevated temperature is also suggested as a means of reducing tendency to crystallisation. Temperatures used are from 260°–325° C. and the duration of the heat treatment varies from ten minutes to eight hours.[44] The addition of 2–5 per cent of fatty soap to rosin is another method suggested.[45] A crystallisable rosin, to which has been added 0·25–1·0 per cent of synthetic resin is claimed to be non-crystallisable.[46] The addition of damar (0·3 to 15 per cent) is also said to be effective in this respect.[67]

Subjection of a film of molten wood rosin to a high voltage discharge in the presence of hydrogen, causes both a reduced tendency to crystallise and an increased melting-point. There is, of course, the possibility of

changes occurring as the direct result of the discharge and because of some hydrogenation.

Effect of Heat.—La Lande has examined the effect of heat on abietic acid from wood rosin over a temperature range of 175°–385° C. for from one to fifteen hours. At lower temperatures anhydrides are believed to be formed, but at higher temperatures decarboxylation becomes more pronounced. The volatile decomposition products include carbon monoxide, carbon dioxide and water. Two different methods of decarboxylation are suggested. In the first, the acid disintegrates into the hydrocarbon ($C_{19}H_{30}$) and carbon dioxide. In the second the acid yields another hydrocarbon ($C_{19}H_{28}$), carbon monoxide and water.[47]

Brodschi has investigated the vapour phase cracking of rosin. Gases were obtained comprising carbon monoxide, carbon dioxide, hydrogen and aliphatic hydrocarbons, together with a liquid with an extended boiling range (30°–200° C.) comprising benzene, toluene and xylene, cymene, cumene, ψ-cumene and cyclohexadiene. A high boiling mixture (above 200° C.) contained anthracene, phenanthrene, retene and naphthalene.[48]

Rosin Oil

The distillate obtained when rosin is distilled is chiefly crude rosin oil, which comprises a mixture of rosin acids and hydrocarbons. The actual composition of the final product is, however, determined by the care taken in the distillation. Decarboxylation of the resin acids is greatly facilitated if the distillation is conducted slowly, or if small amounts (0·5 to 2·0 per cent) of calcium carbonate are present.[20]

The crude oil is also usually washed with alkali to further reduce its acidity, and may be redistilled. Rosin oils with zero acidity are possible. Crude rosin oil is sometimes known as kidney oil. Rosin oil is a pale yellow to reddish-brown viscous liquid with a specific gravity of 0·945–1·000.

Its chief value lies in its great penetrating property and this is exploited in varnishes for window envelopes and in impregnated paper for insulating purposes. It sometimes forms the basis of certain types of printing ink.

During the war, because of its drying properties, it has been employed as a linseed oil substitute, and a component of emulsion paints.

Routine Testing

Because of its cheapness rosin is rarely adulterated. A routine laboratory examination would include tests for colour, clarity, acidity, solubility in white spirit, alcohol, and drying oils, and tendency to crystallisation. If the rosin is to be used for special purposes such as the production of limed rosin, ester gum, maleic anhydride resin, or modified phenolic resin, its behaviour during the formation of these products should be investigated critically, and the properties of the resultant products such as solubility, etc., should be checked.

Palkin and Smith have recorded simple methods for assessing the crystallising tendency of rosin. The time necessary for crystals to develop at 100°–105° C. is noted. The rosin may be dissolved in an equal volume of drying or mineral oil and the time necessary for crystals to develop recorded under these conditions. The crystallisation test is best conducted in a flat-bottomed copper vessel. Alternatively, a test tube is filled with rosin lumps which are covered with acetone. If the rosin has a tendency to crystallise, crystals will separate within an hour.[49]

It is interesting to note that in the determination of saponification value of rosin, the value increases with molecular weight of alcohol used as solvent.[50]

Rosin Modifications

Chemically Activated Rosins.—Rosins containing a trace of catalyst, which are specially reactive with glycerol, lime, litharge, etc., are marketed. The amount of catalyst present is claimed to be too small to affect other properties adversely.

Polymerised Rosin.—Apart from the modifications of rosin already mentioned such as conversion to metallic soaps or esters, others have been made. The unsaturated nature of rosin makes polymerisation under certain conditions possible, and this property has been exploited in the manufacture of polymerised rosins on the large scale. It is now possible to polymerise rosin to the dimer stage to yield a product with a melting-point of 176° C.,[70] which will be available shortly, but the present commercial product is a mixture of polymerised and unpolymerised rosin. The polymer is present to the extent of 30 to 40 per cent. Polymerised rosin has been produced by treating a solution of rosin with boron trifluoride below 50° C.[51] The duration of the treatment varies from five to 120 minutes. Another polymerising agent is concentrated sulphuric acid. A solution of rosin in a monocyclic aromatic hydrocarbon is treated with concentrated acid at − 10°–65° C. The solution of polymerised rosin is separated from the acid, and the polymerised rosin is recovered by evaporation of the solvent.[53] In place of the aromatic hydrocarbon a volatile halogenated organic solvent, which is stable to concentrated sulphuric acid, may be used.[54] Using a petroleum hydrocarbon as solvent for the rosin, the solution is treated with 81 per cent. aqueous sulphuric acid at a temperature between 0° and 40° C. Since the reaction occurs with evolution of heat, cooling is necessary.[55] The heat treatment of rosin in the presence of a minimum of 2 per cent of a mono alkali sulphate or phosphate also affects appreciable polymerisation.[75] Other polymerisation catalysts include anyhdrous hydrofluoric acid, fluoboric acid, and dihydroxyfluoboric acid.[66]

Rosin esters are catalytically polymerised by identical means.[73] There seems to be practically no end to the possible modifications of rosin, for patents have now been taken out covering the hydrogenation of polymerised rosin or its esters in solution under pressure. Hard products of improved resistance are claimed.[74]

Polymerised rosin has an acid value rather lower than that of rosin itself but its melting point is appreciably higher.[52] Other properties claimed for polymerised rosin are improvement in colour and solubility.

The improvement in solubility is demonstrated in solutions which do not crystallise, although by comparison with similar solutions of gum rosin they have a higher viscosity. These properties are also possessed by esters or metallic soaps of polymerised rosin.

According to Cahall (*loc. cit.*), polymerised rosin contains a trace of melissyl laurate and this separates as a flocculent precipitate from alcoholic solutions.

Polymerised rosin has a lower degree of unsaturation than its parent material, and tends to oxidise less.

Polymerised rosin is destined to have an important future in varnish manufacture. Exceptional outside durability can hardly be expected for it, but it is already used, as the calcium soap, in substantial quantities, in interior finishes. Polymerised rosin gives varnishes with harder films and improved water and alkali resistance, by comparison with similar gum and wood rosin products.

It yields hard pale ester gums and is valuable for the production of both maleic anhydric and modified phenol formaldehyde resins of improved properties.

Polymerised rosin blends with shellac, spirit Manila, zein, ethyl cellulose, and most of the commoner varnish constituents.

Hydrogenated Rosin.—Hydrogenation of rosin has been attempted with the object of reducing its tendency to oxidation and discoloration.

Hydrogenation is accomplished using hydrogen at 200 to 15,000 lb. per square inch pressure at elevated temperature in presence of a base metal catalyst. The treatment is continued until the resin has become at least half saturated.[56] Hydrogenation catalysts suitable for use with abietic acid or abietyl alcohol include platinum, palladium, nickel and copper chromate.[57] Heat or alkali activated granulated nickel-aluminium or nickel-silicon alloys have also been suggested as satisfactory catalysts.[71]

Under commercial conditions hydrogenation does not go to completion; on a basis of two double bonds, saturation occurs to about 60 per cent. of theoretical.

Hydrogenated rosin has been vacuum distilled to yield an almost colourless resin.[58]

The composition of hydrogenated rosin has been given by Cahall [70] as follows :

	Per cent
Lactonisable dihydro resin acids	60
Tetrahydro resin acids	14
Dehydroabietic acid	7
Abietic type resin acids	3
Unidentified resin acids	7
Neutral material	9

All the resin acids which have been identified have a triple ring or a phenanthrene nucleus.

Apart from a reduction in the tendency to oxidise, hydrogenation of rosin modifies its properties in several other ways. A certain amount of degradation occurs during hydrogenation, resulting in the formation of a small quantity of material of low melting-point. This has the effect of reducing the melting-point of the final resin slightly below that of ordinary rosin. Although hydrogenated rosin retains its colour on exposure to light and air at normal atmospheric temperatures, loss of colour occurs on heating.

Hydrogenated rosin is soluble in aliphatic and aromatic hydrocarbons, and in alcohol, and is compatible with most varnish making oils and resins.

Solutions containing a high percentage of the resin (40 per cent or higher) crystallise on storage, but when used in admixture with polymerised rosin, Manila, damar, shellac or zein, this tendency is considerably reduced.

Hydrogenated rosin can be used for most of the purposes where gum or wood rosin are used, with the advantage of colour retention; for example, in the preparation of resinates and ester gums; but it is of little value for the production of maleic or phenol formaldehyde resins by reason of its low degree of unsaturation.

Oxidised Rosin.—Rosin can be oxidised by blowing air through it. Experiments have been recorded in which molten rosin is blown with air in the presence of 1 per cent of cobalt oxide (CoO). Substantial increase in melting-point was obtained depending upon the duration of the treatment. Blowing caused a marked increase in the amount of material insoluble in petroleum ether (from 18 to 46 per cent); a reduction of acid value from 159·6 to 145·3, and a reduction in saponification value from 170·0 to 161·3.[59]

A resin has become available in recent years under the name "Vinsol." It is a highly oxidised rosin. It is composed of oxyabietic and other resin acids, with normal abietic acid and polyphenols. It is insoluble in many of the normal rosin solvents and because of its general insolubility it was given the name "Vinsol" which is said to be derived from "very insoluble." Vinsol is insoluble in petroleum hydrocarbons such as white spirit and petrol, turpentine, carbon tetrachloride, and carbon disulphide. It is not very soluble in drying oils even on cooking. It dissolves easily in alcohols, ether, Cellosolve, chloroform, ethylene dichloride, acetone and esters. Solutions can be obtained in toluene if the concentration of resin is high. It is claimed that the resin can be rapidly cooked into tung oil, but the best method of obtaining linseed oil type varnishes is to react the resin with drying oil monoglycerides. The varnishes obtained are very dark in colour and have inferior dry, but are stated to have good durability.

The resin is a dark reddish-brown colour, has a melting-point of 115° C., saponification value of 158 and acid value of 100. Although the resin is brittle it can be plasticised with castor oil. Because of their high

dielectric strengths, "Vinsol" resins are used in the spirit type of air-drying insulating varnish. Other uses for these resins are spirit varnish stains, nitrocellulose lacquers, spirit chassis blacks, asphaltum emulsions, printing inks, core binds, filler media, alkyd and other resins, and lacquers for resistance to petrol and oil.[60]

Dehydrogenated Rosin.—The unsaturation of rosin can be reduced by a process of dehydrogenation in the presence of suitable catalysts.[72] A commercial product containing 50 per cent dehydroabietic acid, 30 per cent dihydroabietic acid and 15 per cent tetrahydro abietic acid is now available.

Dehydrogenated rosin has a slightly higher melting-point than hydrogenated rosin, good resistance to oxidation, and has a pale colour. Its high acid value makes it suitable for the production of glycerol and other esters, or for metallic soaps.

Other Modifications.—A protected process is described whereby rosin is modified by heating with dry formaldehyde, paraformaldehyde or hexamethylene tetramine at 120°–150° C. The product is heated subsequently under vacuum at 230° C. in the presence of a catalyst. The modified rosin produced is harder than the base resin and has a higher melting-point. It yields solutions of higher viscosity. It has no inhibiting effect upon the drying of linseed oil.

Rosin may be condensed with benzyl chloride using zinc chloride as catalyst. The product may be esterified with glycerol if desired.[61] The melting-point of rosin is increased by grinding with bleaching powder. After allowing to stand for ten to fifteen days in absence of air, the calcium salts are removed by washing and the product heated to 150°–200° C.[62]

Uses

Rosin is a very versatile raw material, and in spite of the fact that it is regarded generally as cheap and inferior it is probably used in more different types of finish or composition than any other raw material. As limed rosin for gloss oils it is used in very large quantities. Gloss oils are used frequently as media for producing cheap quick air-drying enamels, or for admixture with oil to yield cheap paint media. Rosin is used in substantial quantities in the production of resinate driers. In conjunction with wood oil, rosin yields good water-resisting varnishes with satisfactory durability. With linseed oil poor drying varnishes with inferior durability are obtained. Rosin is an important component of synthetic resins, being used with phenols and formaldehyde either as rosin or in the form of ester gum. It reacts with maleic anhydride to produce maleic resins and is used in alkyds for the production of rapid air-drying varnishes where speed of set and dry are the chief considerations. Rosin is used as a peptising agent for the reclamation of wood oil gels or as a flux in solubilising difficultly soluble resins. Either alone or with lanoline, rosin forms the basis of rust-preventing solutions which can be removed easily by white spirit or paraffin. Rosin is used in

stantial quantities with spirit Manila in spirit varnishes of many types, although the amount of rosin it is possible to introduce is limited by solubility considerations. Rosin will be found as a cheapening agent in many compositions employing expensive synthetic resins.

CONSTANTS OF SIMPLE AND PROCESSED ROSINS

Reference	Remarks	M. Pt.*	A.V.	Solubility	Uses
Gum rosin	..	58° C. (capillary)	160–172	C.S. aliphatic and aromatic hydrocarbons, alcohols, and most varnish constituents	Cheap varnishes and media, gloss oils, resinates, ester gum, synthetic resins
Wood rosin	..	53°–63° C. (capillary)	150–168	As gum rosin	As gum rosin
Staybelite resin A. 2	Hydrogenated rosin	71·5° C. (Hercules' drop method)	162	As gum rosin. Tendency to crystallise from solution at high concentrations	Ester gums, modified synthetic resins, resinates, adhesives. Practically non-yellowing
Dehydrogenated rosin		Slightly higher than hydrogenated rosin	High	As gum rosin	To substitute hydrogenated rosin
Polymerised rosin		77° C. (capillary)	135–164	As gum rosin, but less tendency to crystallise	As gum rosin, but products are generally harder
Vinsol rosin	Oxydised rosin	111° C. (Hercules' drop method)	98	C.S. alcohol, esters, P.S. aromatic hydrocarbons, I.S. drying oils, turpentine. P.S.H. drying oils	Insulating varnishes, spirit varnishes and stains, nitrocellulose lacquers, asphalt emulsions

* Melting-points by the drop method are approximately 20° C. higher than those of the capillary method.

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Tall Oil

Tall oil was just beginning to become popular at the outbreak of the war. After several years of war it has definitely established itself as a raw material in certain types of paint and varnish products. This is especially true in the United States of America, on the Continent of Europe and in the U.S.S.R. In Great Britain, on the other hand, it is still known, to the majority, by name only.

Production.—Tall oil is a rosin product known also as "Tallol" or liquid rosin. It is a by-product of the paper pulp industry using the sulphite process, and is obtained by hydrolysis of soaps of the alkaline waste liquors. It may be a tarry viscous liquid, with a strong smell, but its colour and smell varies, especially if it has been subjected to refinement.

Tall oil melts about — 20° C. and has a boiling-point of 270° C. at 40 mm.[1] The actual composition of raw tall oil varies considerably. It contains unsaturated acids of C_{18} type, rosin acids, and unsaponifiable matter. A rough idea of the composition and properties of tall oil can be gleaned from a consideration of the properties of the components of a suggested substitute. This consists of a mixture of rosin oil containing a substantial amount of abietic acid, with vegetable oil fatty acids, e.g. oleic, linoleic, etc.[13]

Purification.—Because of its variable composition and certain disadvantages its purification has attracted much attention. Refined odourless tall oil is obtained by heating at 150° C. under vacuum, and passing steam through it. Impurities may be deposited during the process and these are removed.[2]

Alternatively, it is refined by ordinary distillation or by distillation with superheated steam under vacuum. The latter process increases the saponification value. Other methods of refining include solvent extraction, for example with petrol or furfural, hydrogenation, or crystallisation.[3] Resin acids are removed from tall oil by crystallisation. Kolke suggests that resin may be removed from tall oil by chilling, and clarification may be effected by three months' ageing.[4]

An American patent claims to separate the fatty acids of tall oil from the resin acids by what seems to be a curious selective esterification process. Alkyl esters of the fatty acids are produced by reaction with methyl alcohol, and the resin acids are converted into metallic soaps. The esters are separated by distillation.[10] A subsequent patent based on the same theory of selective esterification describes the use of crude wood alcohol in the presence of hydrochloric acid and formaldehyde. Upon the addition of water an insoluble ester-resin acid complex separates.[11]

Uses

Tall oil to which the usual driers are added, dries, in time, to a brittle film and it is not surprising therefore, that its drying properties have stimulated the interests of formulators. They perceived in tall oil a cheap film-forming substance, possibly replacing in part, both the drying oil and the resin of varnishes. Tall oil has been vulcanised with sulphur chloride, and oxidised by blowing at elevated temperatures.

But untreated tall oil does not appear to have been used much as such, except perhaps in the manufacture of modified alkyd resins and in some rust-proofing paints. These are claimed to have good durability, and best results are obtained with one part of alkyd to four parts of linseed stand oil. Composite alkyds containing tall oil, and sunflower, soya bean, or cottonseed oils have also been prepared, and these have yielded satisfactory varnishes and enamels.[12]

An alkyd resin which forms the basis of an air-drying varnish contains tall oil 36·36 per cent, semi-drying oil 11·23 per cent, phthalic anhydride 33·1 per cent, and glycerol 19·31 per cent. The resultant varnish dries well and possesses good durability, water and oil resistance.[14]

Tall oil fatty acid modified alkyds are compatible with nitrocellulose.[4] Tall oil can be used in rust-proofing paints with red oxide of iron, but not with basic pigments.[5]

With the above exceptions, it is the products from modified tall oils which have been found most valuable generally.

Tall Oil Esters

If the fatty acids present in tall oil are esterified, a product is obtained with drying properties. The drying rate is not so good as that of most of the common drying oils, in fact, the glycerol ester requires seventy-two hours to set to a solid film with added drier. The tall oil esters are therefore most satisfactory in admixture with better drying oils.

Results of work on mixed stand oils conducted by Niesen has been recorded.[15] Stand oils were made from mixtures of equal parts of tall oil esters and linseed, perilla, tung and oiticica oils, and a strong influence in retarding heat polymerisation was observed. Varnishes of alkyd or phenolic character were prepared from these oils but the properties were disappointing. Drying rate was slow, and except for the tung oil

varnishes, the water absorption was exceptionally high. Embrittlement on ageing occurred with the alkyd varnishes.

There is evidence, however,[7] that when the pentaerythritol or glycerol esters of tall oil are used alone with alkyd resins that improved durability and drying are obtained. Copal ester, ester gum and certain other synthetic resins are also stated to effect some improvement in the durability of tall oil esters. Esterified tall oil fatty acids have been used as a linseed oil substitute in rust-proofing paints. A medium consisting of a mixture of one part of tall oil ester with four parts of linseed oil is claimed to give adequate rust-proofing for about four years.[9] But it is a moot point that this evidence is strong enough to merit their wholesale adoption for durable exterior finishes. Their elasticity is inferior to that of linseed, tung and oiticica oils. As with most vegetable and other types of drying oils careful processing and formulation are necessary for the best results; this has been shown to be very true of oiticica oil—a relative newcomer to the field. The same contention, is, no doubt, also equally true of tall oil esters. Thus where durability is of prime importance, tall oil esters are used with caution. Nevertheless, they can be used in many types of short oil interior finish, with the advantage of cheapness.

Varnishes produced from tall oil esters yellow rapidly, and the esters themselves are generally much darker in colour than the normal drying oils and possess more unpleasant odours. The acidity of the esters can be reduced sufficiently to permit use with basic pigments.

The free fatty acids of tall oil may be esterified with glycerol, pentaerythritol, phenol or ethylene glycol.[5]

Reinert states that the presence of resin acids in tall oil is advantageous for most purposes and, therefore, they are not removed as a matter of course.[8]

Tall Oil Soaps

It is not unreasonable because of the acidic nature of tall oil that it has been used for the preparation of metallic soaps. Among the neutralising agents used for this purpose may be included the oxides of calcium, lead, magnesium, and zinc, and the usual inorganic compounds of cobalt, manganese and iron commonly used in the manufacture of driers.

Westgate advocates the treatment of tall oil with 5 per cent of lime at 280° C. for thirty minutes to obtain a product of improved drying properties and flexibility.[16] Or raw or distilled tall oil is blown at a comparatively low temperature (80°–200° C.) for about forty hours, bodied for about ten hours at a higher temperature (250°–300° C.), and then subsequently neutralised with lime.[17]

Reaction with metallic compounds is also effected as a second stage to the esterification process.

A tall oil product with good drying properties is made by first reacting together tall oil (58 per cent); rosin (28 per cent); and glycerol (14 per

cent); and the intermediate product formed is then neutralised with lime (1 per cent) and litharge (0·4 per cent).[18]

Complex metallic soaps are also prepared by esterifying the tall oil with 2–7 per cent of a monohydric alcohol of which butyl alcohol or cyclohexanol are typical. Oxides of zinc, lead, or calcium, are next added at a higher temperature, and the heating continued until the acid value is reduced to 35 or lower. The product can be used as a medium with zinc oxide without a tendency to feed.[19]

The lime soaps of tall oil are used as gloss oils. The iron soaps have found application in stoving varnishes. The cobalt, manganese, and lead soaps are satisfactory driers, whilst the soaps of the alkaline earths possess good wetting and dispersion properties.

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CHAPTER 5

NATURAL SPIRIT VARNISH RESINS

SHELLAC

ALTHOUGH shellac is not used in the varnish trade in such large quantities as other natural and synthetic resins it has attracted a considerable amount of interest. Much research and development work has been done.

Source.—Lac is the secretion of an insect, *Laccifer lacca*, which swarms on the twigs of special trees. A comprehensive list of host trees is given by Parry.[1]

The insects extract sap from the twigs but its constitution and the nature of the process involved for the production of lac are not completely understood. Gibson [2] suggests that if the food for the lac insect could be produced synthetically, the insect could be cultivated under ideal conditions.

The greater part of the world's shellac supply comes from India. Assam, Burma, Indo-China and Siam supply smaller quantities. Attempts have been made to produce lac in Abyssinia. Two crops of lac are produced yearly. Climatic influences seem to alter the properties of the lac produced. In the areas west of Calcutta lac has a yellow or orange colour; in Assam it is pale red, and dark red in Siam.[3] Other variations in properties may be due to the type of host tree, the time of the crop and the district, species of lac insect and method of cultivation. Shellac as used by the varnish trade may vary in properties for various reasons, including method of production and time of storage.

Production

Sticklac.—The incrusted twigs are scraped to remove the lac and this crude product is known as sticklac. The twigs may be scraped with knives, twisted by hand to remove the incrustation, or crushed in mills. Sticklac tends to become insoluble on ageing so that it is converted to seedlac rapidly. Parry [4] notes that deterioration of sticklac may arise from the fermentation of sugars, animal debris or proteins, or from the evolution of ammonia.

Seedlac.—Seedlac is obtained from sticklac by crushing and separating the crushed product into wood splinters, dust and larger lac particles. Water-soluble impurities are removed by agitation in water, which serves also to remove dye, and the resultant product when dry becomes the seedlac of commerce. Lac is used in the form of seedlac in substantial quantities. Seedlac tends to polymerise on storage. Constancy of quality of finished shellac is achieved by blending different grades of seedlac before further processing.

Shellac.—Lac in the form of thin flakes is known as shellac. This

may contain orpiment (arsenic trisulphide), the sole function of which is to mask the colour of the original shellac. It has been stated that its introduction is valueless and useless.[5] Rosin may be added to shellac during manufacture up to 20 per cent. by weight. T.N. shellac contains up to 3 per cent of rosin.

Shellac is produced from seedlac by mixing it with rosin and/or orpiment if these adulterants are used at all, and the material transferred to calico bags and subjected to a cooking process. The filtered mass obtained, when plastic, is stretched into thin sheets from which common shellac flakes are derived.

Garnet lac.—Garnet lac is similar to shellac except that it is usually darker in colour, is free from wax, and appears on the market in thicker flakes ($\frac{1}{8}$ in.). It is manufactured principally from Kirie, which is the residue remaining from the filtration of molten seedlac.

Button lac.—Button lac is manufactured by a similar method to that for shellac except that no stretching occurs and the molten lac is allowed to fall in small quantities on to flat surfaces.

Dewaxed Shellac.—Ordinary shellac contains about 3–5 per cent of wax. If shellac is dissolved in industrial alcohol the solution obtained is turbid, due to the wax which does not dissolve but remains in suspension. The wax may be allowed to settle or removed by filtration. Wax is removed from shellac by extraction with aromatic hydrocarbons such as benzene, toluene and xylene in the presence of water. The water is claimed to prevent polymerisation of the shellac.[6] The wax may be precipitated from an alcoholic solution of shellac by the addition of water. The clear filtrate may be worked up for wax-free shellac. Another method is to dissolve the shellac in aqueous sodium carbonate, filter off the insoluble wax and liberate the wax-free shellac by addition of acid.

Dewaxed shellacs are obtainable by these means and yield thinner and more transparent solutions. Rosin and orpiment are absent. The advantages assigned to dewaxed shellacs over bleached shellacs are that they have better tensile strength and solubility.[7]

Bleached Shellac

Special pale grades of shellac are produced. These are known as bleached shellacs, obtained by chemical treatment, and as decolorised shellacs produced by special processes. The latter are claimed to be free from the defects of the chemically bleached product. It is further claimed that the decolorised shellacs retain all the properties of the original natural lac.

Lac is bleached by dissolving in a hot 2 per cent solution of sodium carbonate. Sodium hypochlorite is then added with constant stirring. The bleaching is a gradual process and the mixture is allowed to stand. The bleached shellac is then precipitated from solution by the addition of sulphuric acid. Excess acid is removed by washing and the plastic mass of shellac is converted into hanks. Chloride of lime and chlorine

are other bleaching agents used. Bleached shellac in the form of hanks contains a considerable amount of occluded water as well as wax. The water may amount to as much as 25–30 per cent. A so-called bone dry grade of bleached shellac is sold and this contains substantially less water, usually about 5–6 per cent.

Selection of Shellac for Bleaching.—Great care must be exercised in choosing a shellac for bleaching. The best grades of seedlac for bleaching are derived from kusum and khair lacs. Lacs from ber and palas hosts are inferior. If the sticklac used as the starting material is stored under conditions such that it tends to "block," it is less satisfactory for subsequent bleaching.[8] Gardner, Koprowski and Murty emphasise the importance of collecting lac for the manufacture of shellac from the tree at correct times, and the necessity for short storage. It should not be left on the host tree after the young insects have swarmed, since polymerisation may occur. When sticklac or seedlac is stored changes occur as evidenced by alterations in both physical properties and chemical constitution. Fluidity of the melted lac decreases and the solubility in boiling acetone changes also.[9]

Amount of Bleach Liquor Required.—Gardner and Harris record that the amount of bleaching liquor necessary varies with the percentage of resin insoluble in hot acetone. When the amount insoluble in acetone is 15·7 per cent, 54 per cent excess of bleaching liquor is necessary. If the amount insoluble is not more than 4·8 per cent no excess is required.[10] Murty records that the nitrogen content of shellac controls the amount of sodium hypochlorite necessary. The amount of hypochlorite also varies with the colour of the initial seedlac. A preliminary washing of crude shellac with a very dilute alkali solution reduces the amount of bleach liquor required. If orpiment is present the time for bleaching is prolonged and the amount of bleach liquor increased. The presence of rosin has no material effect.[11] Rapid bleaching tends to induce insolubility. After the hypochlorite has been used up further prolonged contact with the alkaline solution results in the colour returning to the shellac. Hydrochloric acid splits off and the unsaturation of the shellac increases. During the bleaching process the chlorine is believed to enter the shellac partly by substitution and partly by addition.[12] If old and polymerised seedlac is used as a starting material for bleached shellac, the product is more brittle than that from fresh seedlac and may need plasticising.

Other Methods of Production.—A bleached shellac in the form of needles, originating in Belgium, has been introduced, and is said to be prepared by a spinning process. Bleaching is obtained by the use of chlorine and chlorine compounds and any shellac is stated to be suitable for conversion to needles.[13] Contradictory reports have been recorded on its stability. Its chief advantage is that it dissolves very rapidly in alcohol, due to its fine capillary structure. It contains less than 2 per cent moisture.[14]

Another method of bleaching shellac electrically has been described. A solution of shellac in a sodium carbonate-sodium hydroxide-sodium chloride solution is subjected to an alternating current for eight to sixteen hours.[15]

Hard Lac Resin.—Another specially manufactured form of shellac which has appeared in recent years is known as hard lac resin. It is sometimes described as pure lac resin.

Its preparation is based on the fact that the soft resin constituent of shellac can be removed by fractional solvent extraction.

The soft resin is soluble in ether and can be removed by extraction. Hard lac resin is insoluble in ether and constitutes about 75–80 per cent of the original shellac.[16]

A works process for the manufacture of hard lac resin has been evolved by the London Shellac Research Bureau.[17] The best results were obtained by solvent extraction, and the solvents studied include naphtha, benzene, toluene and trichloroethylene.

Hard lac resin may be obtained also by dissolving shellac in alcohol to which chlorinated or aromatic hydrocarbons are added. Addition of water causes the precipitation of the hard resin, leaving wax and soft resin in solution.[18] Two further methods of preparation are described by Venugopalan and Sen.[19] Shellac or seedlac (40 pts.) is dissolved in acetone (60 pts.), 7–8 per cent of urea, calculated on the shellac is added, and the whole left until gelation occurs. This usually happens within four days. The residue from the gel after acetone extraction is polymerised hard lac resin. After depolymerisation with boiling water it is dried under vacuum. Alternatively, a solution of shellac is prepared in acetone or in an acetone-benzene mixture and stirred at a low temperature (0°–5° C.) for thirty minutes until gelation occurs. The soft resin is separated from the hard resin by squeezing through muslin. According to Bhattacharya, hard lac resin can be obtained by means of aqueous sodium pyrophosphate. Its use is claimed to be cheaper than extraction with organic solvents.[20]

Many claims have been made in favour of hard lac resin against ordinary shellacs. Hard lac resin is said to have better water resistance, polymerises more readily under heat, has better adhesion, flexibility, gloss, durability, scratch hardness; and better compatibility with drying oils, alkyds and nitrocellulose; almost complete elimination of solvent retention, superior heat resistance and a higher melting-point. Cold hardening of hard lac resin may be accomplished by the addition of urea. Some grades of hard lac resin available on the market need special treatment to obtain a solution in alcohol. Concentration of the lac seems to be fairly critical. It is recommended that a 30 per cent solution be prepared first and this is then thinned out with further alcohol. At concentrations of less than 15 per cent lac precipitation may occur. The addition of a few per cent of white spirit to an alcoholic solution of hard lac resin is said to yield harder films on drying.

Machine-Made Shellacs

The age-old "native" refining process cannot produce highly specialised types of shellac to suit the more specific requirements of modern industry. These demands are met by the development of the so-dalled "machine-made" shellacs.

The processes employed fall into three main headings :—

(*a*) Mechanical adaptations of the "dry" native process ;

(*b*) Pressure filtration in the presence of steam ; and, most important of all,

(*c*) Solvent extraction.

Each of these imparts particular characteristics to its products.

Composition of Shellac

Chemical Constitution of Components.—A chemical examination of lac reveals the following components : extraneous matter comprising twigs, wood, bark, mineral dust, sand, pieces of charcoal, insect carcases, etc., lac dye and water soluble material, wax, soft lac resin (ether soluble), and hard lac resin (ether insoluble). Karim points out that the impermeability of plastic shellac to solvents makes separation of the components difficult.[21]

Other materials present in shellac which are added subsequently include orpiment (0·2–0·5 per cent) and rosin. Gardner and others have shown shellac to be a blend of constituents. Bhattacharya states that lac resin comprises, among other constituents, hydroxy acids, and of these two have been isolated. One is a trihydroxy palmitic acid (aleuritic acid) and the other is believed to be a dihydroxy hydroaromatic dibasic acid (shellolic acid). Other unidentified unsaturated acids are also present.[22]

According to Parry, shellac contains about 30 per cent of aleuritic acid, 10 per cent of shellolic acid, and the remainder consists of colouring matter, etc.[23]

The chemical constitutions of the components of shellac have been investigated by the following workers : Tochirch and Farner, Harries and Nagel, Endemann, Nagel, Ulzer and Defris, Indian Lac. Res. Inst., Nagel and Mertens,[24, 25] Bhattacharya,[26] Verman,[27] and Gidvani.[91]

Modifications of Shellac

Modifications of shellac have been made. Shellac is heated at 180° with 3 to 4 per cent of sulphur. The product obtained is greenish in colour. It has better adhesion, elasticity, toughness and water resistance than the original shellac.[28] If sulphur chloride is added to a solution of shellac in carbon tetrachloride its water resistance is reduced.[29]

The addition of a fractional percentage of concentrated hydrochloric acid to an alcoholic solution of shellac causes appreciable modification in properties. The film obtained dries more slowly, is matt and has

poor adhesion under moist conditions. Corrosion of the container also occurs.[30]

Dry zinc oxide (10–7 pts.) and dry shellac (10–13 pts.) are heated together at 120°–280° C. to yield a compound.[31]

A large amount of work has been conducted on the modification of shellac with urea or thiourea and it is believed that chemical combination occurs. The addition of small percentages of these substances to shellac solutions promotes substantial increases in viscosity on ageing. Shellac treated with 2 to 3 per cent of these substances shows an improvement in hardness, abrasion resistance, water resistance, elasticity and adhesion. The results obtained are not so marked with thiourea as with urea. The heating of shellac with urea or thiourea improves its heat resistance.[32] Etherification of shellac can be accomplished by interaction with mono or poly alcohols, of which ethylene glycol is typical. The reaction products yield tough flexible resins on heating.[33]

Gidvani and Bhattacharya have reported the formation of an ether from shellac and ethylene glycol in which only one hydroxyl group of the glycol is involved. The remaining hydroxyl groups are reacted with drying oil fatty acids. Rubbery products are obtained on heating the resultant resins at 120°–135° C.[34]

Esters can be produced from shellac by interaction of its hydroxyl groups with acids. Three of the hydroxyl groups react more readily than the other two. Resins which air dry or stove are obtained from the esters of high molecular weight unsaturated acids. If careful control is exercised, esterification of each of the five available hydroxyl groups can be accomplished separately. Bhattacharya and Gidvani have studied the esters of shellac, derived from the following acids: acetic, caprylic, stearic, lauric, oleic, rosin and linseed oil fatty acids. The progress of esterification is followed by determinations of acid and hydroxyl values.[35]

When shellac has been etherified with ethylene glycol, esterification of the free hydroxyl groups can be brought about by means of unsaturated acids. A range of polymerisable resins is obtained.[33] The methyl and butyl esters of shellac are used in cellulose lacquers.[36] Esters have been prepared from shellac and rosin in the presence of castor oil or phenol.[37]

A reaction occurs when shellac, fatty acids and glycerol are reacted together in the presence of a catalyst. Monoglycerides are formed initially and these react subsequently with the hydroxyl groups of the shellac. Under favourable conditions the carboxyl group of shellac reacts with monoglycerides.[38] Shellac in its various forms has been hydrogenated at ordinary temperatures using Raney nickel as catalyst.[39]

Valuable products are claimed from the interaction of maleic acid and an alcoholic solution of shellac if refluxed.[40]

One molecule of shellac is found to absorb six molecules of sulphur dioxide. The sulphited products are said to be commercially useful.[41]

Shellac Substitutes

From time to time shellac substitutes have appeared, but generally they do not possess the characteristic properties which one associates with shellac. Some substitutes are on a phenol formaldehyde basis. Schreiber and Noack claim that a shellac substitute is derived from linseed oil fatty acids and soft Manila resin acids. The acids are blended, oxidised by means of potassium permanganate and heated at 150° C. to yield an alcohol soluble resin of melting-point 90° C.[42] Harries and Nagel have recorded experiments on the synthesis of shellac.[43] A shellac substitute is claimed by adding sodium carbonate in quantity just less than that necessary to neutralise the free acidity of Pontianac gum, dissolved in a solvent comprising equal parts of alcohol and toluene. A similar method is described whereby an alkali or alkaline earth compound with basic properties is added to a solution of Pontianac or soft Manila in a mixed solvent of ethyl alcohol and toluene. To 250 parts of resin, less than eight parts of alkaline compound are added.[44] Another shellac substitute is claimed in a fused blend of equal parts of rosin and accroides.[45]

Pine needle resin, indigenous to Brazil is suggested as a partial shellac substitute. It may be used in equal amounts with genuine shellac. It is almost completely soluble in hot alcohol, only 1·7 per cent remaining insoluble, and has a m.pt. of 105° C.; A.V. 22; S.V. 156·5; and I.V. 27.[89] Zein is possibly one of the best shellac substitutes and is considered in a section devoted to it on page 141.

Analysis and Testing

The analysis and testing of shellac is important. From the varnish makers' point of view the following tests are necessary :—

Colour.—Colour of shellac should be determined by dissolving the shellac in industrial alcohol and comparing the colour of the solution obtained with that of a standard sample prepared similarly, or by filtering the solution to remove suspended matter. The clear filtrate obtained may be compared with a range of colour standards consisting of solutions of iodine in potassium iodide. Zoellner suggests that colours of shellac solutions can be matched against solutions of caramel containing precipitated chalk in suspension.[46]

Rosin. Qualitative and Quantitative Analysis.—Since adulteration of shellac with rosin is always a possibility in view of the marked difference in price of these resins, the detection and estimation of rosin is important. Rosin in shellac may be determined qualitatively by application of the Halphen-Hicks test, although the test is unreliable for bleached shellacs.[47] The Liebermann-Storch test also gives satisfactory results for rosin in shellacs. Another method for the detection of rosin is by means of copper acetate. Parry describes the method whereby 1 gram of shellac is dissolved in 25 c.c. alcohol. The resin is obtained in a finely divided form by pouring the alcoholic solution into a large quantity of water

which causes precipitation. The precipitate is dried and shaken with petroleum ether to extract the rosin. A 1 per cent aqueous solution of copper acetate is shaken with the petroleum ether extract. The presence of rosin is indicated by the development of a green colour in the petroleum extract.[48]

Rosin may be estimated quantitatively by two methods: solvent extraction and iodine value determination. Both methods are open to criticism and the results obtained should be used with caution. Shellac in its original condition or even in the form of a fine powder is relatively impervious to the action of solvents and the rosin is not easily extracted. Further, there are always complications due to the fact that the solvent used to extract the rosin tends to dissolve out the shellac wax and other substances. The shellac is obtained in a favourable condition for extraction by dissolving it in aqueous sodium carbonate solution and removing the insoluble wax by filtration. The filtrate is acidified and the shellac precipitated in a finely divided condition for subsequent extraction.

The following extraction method is due to McIlhiney[49]:—

Two grams shellac are dissolved in 20 c.c. absolute alcohol by warming. After cooling, 200 c.c. of petroleum ether are added and the mixture vigorously shaken. 100 c.c. of water are added and the mixture again shaken. The mixture is filtered through 120 mesh wire gauze into a separating funnel. The petroleum extract is separated and washed once with 20 c.c. dilute alcohol (1 part alcohol, 5 parts water). The clear filtrate of the petroleum extract contains wax and rosin.

The rosin is removed by extraction with 25 c.c. N/5 alcoholic caustic soda. The lower layer is run into an evaporating basin.

A blank is prepared by titrating 25 c.c. N/5 alcoholic caustic soda with N/10 hydrochloric acid. The mixed solution is evaporated to constant weight. The alcoholic caustic soda solution containing rosin is titrated similarly with hydrochloric acid using phenol phthalein as indicator. The amount necessary for neutrality is noted and the amount of acid added is increased up to that used to neutralise 25 c.c. alcoholic caustic soda. The mixture is evaporated to constant weight as before and the difference between this weight and the blank weight gives the weight of rosin acids extracted. From the titrations and the weight of rosin extracted it is possible to deduce the acid value of the rosin acids. Since, according to McIlhiney, about 2 per cent of soluble acidic material is extracted from pure shellac and that extraction of rosin is completed only to the extent of 83 per cent, the figure obtained for the percentage of rosin present must be adjusted.

100/83 (per cent rosin acids − 2) = adjusted percentage of rosin. When very small percentages only of rosin are present, i.e. of the order of 2 per cent, the method has not sufficient accuracy.

The petroleum extract separated in the above method, as already indicated, contains shellac wax, together with a small percentage of soluble

matter from the rosin. This is evaporated to constant weight to give the amount of wax present. A correction by deduction based on 10 per cent of the rosin present should be made for the other soluble matter present.

Rosin may be estimated also by an iodine absorption determination. The method is based on standards for the iodine absorptions of shellac and rosin and this may cause unsatisfactory results. Further, in deciding upon standards for shellac and rosin on which to base calculations, it is essential that the standards chosen are derived by the same method as that used for the actual iodine absorption determination of the shellac. To illustrate this, the iodine values for rosin and shellac based on the Wijs-Langmuir method are 228 and 18 respectively,[50] or for the Hubl method, 125 and 10 respectively. The presence of orpiment in shellac causes abnormally high iodine values. Parry and Ferguson confirm this both for Hubl or Wijs methods and state that high iodine values may lead to the erroneous conclusion of the presence of rosin.[51]

Solubility.—Solubility of shellac is a property which must be checked carefully since ageing produces insolubility. The precise duration of exposure of shellac to produce insolubility is still somewhat controversial. One authoritative Indian source states that shellac becomes insoluble in cold alcohol after two years' storage under Indian conditions,[52] whilst an equally authoritative source states that in well-ventilated warehouses at low temperatures and humidity, seedlac shows no deterioration in two years, and shellac keeps in good condition even longer than seedlac.[86] The answer to this apparent contradiction lies in the severity of the storage conditions. It is the author's experience that a few months' storage of shellac under natural Indian conditions produces changes in the material such that it becomes extremely difficult, if not impossible, to incorporate it into hot vegetable oil or monoglycerides. In normal times, the distributors of shellac in India store it under conditions of cold storage, and even take the precautions of shipping it under similar conditions.

The percentage of shellac insoluble in cold 95 per cent alcohol after one hour's mechanical agitation is a good indication of the quality of the shellac. Refluxing will cause old shellac to dissolve into solution. Total impurities in shellac (dirt, etc.) may be regarded as the percentage material insoluble in boiling alcohol.

Old shellac is also difficult to filter as an alcoholic solution,[87] and shows a reduced fluidity on heating and unusual thermosetting characteristics.

Shellac has always commanded a comparatively good price for a raw material and it is not surprising that research has been performed on its regeneration after deterioration. Precise details of a method of regeneration have been given in a publication of the London Shellac Research Bureau,[86] but in general, the process consists in heating the blocked or deteriorated shellac with sodium carbonate (4·5 to 5 per cent) or hydroxide (10–15 per cent), using just sufficient water to give a fluid

mass. Temperatures of 105° ± 5° C. are suggested, and the duration of the treatment depends upon the degree of deterioration of the shellac. Acidification with dilute mineral acid sets free the shellac.

In cases of slight deterioration, submersion in water will often regenerate solubility in alcohol.

Orpiment. Qualitative and Quantitative Analysis.—If orpiment is present in shellac this may be detected qualitatively by dissolving the shellac in alcohol and allowing the solution to settle. The orpiment will settle out as a yellow precipitate. Alternatively, arsenic may be detected by the usual chemical means.

The arsenic in shellac may be determined quantitatively by a method due to Langmuir and White.[53] The organic matter in shellac is decomposed by boiling 2 g. with 15 g. of potassium sulphate and 50 c.c. of concentrated sulphuric acid. Arsenic sulphide is precipitated by passing hydrogen sulphide through a dilute acid solution. The precipitate is removed, dissolved in ammonium carbonate and reprecipitated by reacidifying. Finally, it is dried and weighed.

Water Estimation.—The determination of water in shellac, especially in bleached shellac, which is liable to contain large amounts, is very important, although the best procedure to adopt constitutes a difficult problem. Shellac contains both free and combined moisture, and the difficulty is to devise a method which will give accurate results for either type of moisture. Temperatures in excess of 100° C. tend to drive off combined moisture, whilst free water is held so tenaciously that low temperatures may fail to dislodge it.[54] Conditions for moisture determination may vary from drying at ordinary temperatures by means of some dehydrating agent to drying at temperatures as high as 120° C. Probably the most satisfactory method for routine testing of bleached shellacs is to dry them in powdered form at 40° C. for a specified time, for example, for four to six hours, and to compare the result with some fixed standard obtained under the same conditions.

Assessment of Bleachability of Shellac.—Although the bleaching properties of a shellac are not the immediate concern of the varnish maker, a few notes on the subject may provide him with knowledge useful in assessing the value of a given bleached shellac. The bleachability of shellac may be obtained by determining the quantity of hypochlorite solution necessary to yield a certain standard of colour. A large shellac manufacturing concern has suggested an alternative method which is claimed to be more satisfactory in practice.[55] The time required to absorb a given amount of hypochlorite is taken as a guide to the amount of hypochlorite necessary. The shellac for test should be ground to 10 mesh gauge; very fine or very large particles must be avoided. 30 g. shellac or seedlac are dissolved at 65° C. in sixty minutes in 150 c.c. of a 2 per cent. sodium carbonate solution. The solution is filtered through a 100 mesh sieve, the insoluble material washed with water and the washings added to the filtrate. The insoluble material can be dried, if desired, to constant weight.

The filtrate is maintained at 40° C. in a water bath, with constant stirring, during the addition of the hypochlorite solution. Fifty c.c. of sodium hypochlorite solution (3 per cent. available chlorine) are added, and the time noted for complete absorption as detected by starch iodide paper. The volume of subsequent additions is controlled by the time occupied by the first absorption. The following data is given :—

Time of absorption.	*Less than* 30 *mins.*	30–60 *mins.*	60–90 *mins.*	*More than* 90 *mins.*
Next addition	20 c.c.	10 c.c.	5 c.c.	Nil.

The time for absorption is again noted and further additions are made on the same basis. The bleached shellac is precipitated from the cold alkaline solution by means of a slight excess of acid (10 per cent sulphuric acid). The precipitated lac is washed free from acid, dried at 40° C., and can be dissolved to yield a 10 per cent solution in alcohol from which colour can be assessed.

Langmuir [56] has recorded that the presence of rosin in shellac increases the quantity of hypochlorite required for bleaching and yields products of inferior colour. The presence of orpiment in shellac during bleaching also necessitates the addition of extra hypochlorite, and Aldis has suggested that the shellac used should be free of this adulterant.[57]

Detection.—Shellac can be detected readily in lacquers or varnishes by the characteristic smell it provides when films containing it are gently warmed. Bhattacharya and Verman have suggested its ready dispersability in sulphurous acid as a means of distinguishing it from other resins.[58] According to Thakur and Aldis a shellac having a refractive index outside the range 1·516 to 1·519 at 23° C. ± 3° must be regarded as abnormal. Curing of shellac for three hours at 105°–110° C. causes no alteration in refractive index.[59] A method for the quantitative separation of shellac acids has been worked out by Schaeffer and Gardner.[60]

Properties

Physical Constants.—Shellac has the following constants : melting-point 75°–85° C. ; specific gravity 1·15–1·20 ; iodine value 13–17 (Wijs) ; and acid value 60–70.[61]

Solubility.—Its ready solubility in alcohol and its hardness, toughness and adhesion makes it a valuable component in quick-drying lacquers for many purposes. Shellac dissolves not only in a wide range of alcohols but also in ethyl ethers of ethylene and diethylene glycols, diethylene glycol, acetic, formic, propionic, butyric and lactic acids, diacetone alcohol, acetaldehyde, aniline and pyridine.

Shellac is insoluble or only partly soluble in most esters, or ketones, and insoluble in glycols, glycerols, aromatic and aliphatic hydrocarbons, carbon disulphide, turpentine and chlorinated hydrocarbons. Shellac is soluble in aqueous alkaline solutions comprising sodium borate, sodium carbonate, sodium hydroxide, mono and triethanolamine, potassium

hydroxide and ammonia. Aqueous solutions of shellac can be prepared in sodium carbonate or borate solutions or in ammonia, containing 15 per cent of shellac. Although initially the solutions may be viscous, there is a tendency to lose viscosity on ageing.[62] The alkalies react with the acids in shellac to form sodium, potassium or ammonium salts.

When wax is present in shellac this remains undissolved both in alcoholic and aqueous alkaline solutions.

Plasticisers.—The following plasticisers have been suggested for use with shellac to improve flexibility; tricresyl phosphate, triphenyl phosphate, tributyl phosphate, tritolyl phosphate, sextol phthalate, heavy pine oil, lac wax, diethyl and cyclohexyl phthalates, elemi, Venice turpentine, and castor oil. Verman and Bhattacharya recommend sextol phthalate as a very good plasticiser for shellac.[63] Another useful plasticiser is a derivative of shellac itself—depolymerised shellac. The material used as a plasticiser is made by heating one part of lac and an equal amount of a 1 per cent soda ash solution in an autoclave at 200° C. for about an hour. Further information on the depolymerisation of shellac is given under Solubility on page 128, and later under Depolymerisation on page 132.

The effect of plasticisation has been studied by the same workers who have recorded these conditions. The addition of plasticisers to films on copper increases adhesion and flexibility but reduces scratch hardness. If the films are stoved scratch hardness increases. Films on tin behave differently in that plasticisation hardly affects scratch hardness. An increase in hardness of films whether stoved or air dried is observed when the plasticiser is increased from 5 to 10 per cent. When lac wax is used as a plasticiser, its addition improves flexibility and scratch hardness. Verman makes the interesting suggestion that the modulus of elasticity calculated from velocity of sound measurements would assist in the elucidation of plasticisation problems.

For many purposes, shellac is used as an aqueous solution, and the problem of plasticising the resultant films needs special consideration. Gidvani has recorded his conclusions on this subject, based on ammoniacal aqueous lac solutions, and they may be summarised briefly as follows. The best plasticisers are Reomol G, stated to be a high boiling ether type phenolic plasticiser, and dimethyl glycol phthalate. The next best are Reomol P, a high boiling phthalic acid ester, and Reomol E which is an alkyl glycol phosphate. Plassitil and diethylene glycol are good where water resistance of the ultimate film is not of primary importance, but glycerine, ethylene glycol, Turkey red oil and triethanolamine are unsatisfactory.

Deterioration on Storage.—Shellac should be stored under cool conditions. As indicated already long storage induces polymerisation and insolubility. This subject has been dealt with in detail in the section devoted to Solubility.

Thermosetting Properties.—When shellac is heated it melts but under prolonged heating thermosetting occurs. Thermosetting or curing is

believed to be due to lactone or anhydride formation.[64] The thermosetting process can be accelerated by the addition of zinc chloride, aluminium chloride, oxalic acid, hexamine or urea, especially at lower temperatures.

Thermosetting is retarded by alkalies and solvents, or if the escape of water is prevented. Ammonia is an alkali, however, which has an accelerating effect. Ranganathan and Aldis have suggested a simple method for the determination of curing time. Molten shellac is heated at a fixed temperature until a glass rod when twisted in the mass, twists in the opposite direction when released. The time taken to assume this condition is noted. Figures given show that shellac requires 227 minutes to cure at 120° C. and only 6·5 minutes at 250° C.

Depolymerisation of Shellac.—Polymerised shellac can be depolymerised by heating with water in an autoclave at 5–20 kg. per sq. cm. pressure for 10–120 minutes. Iodine and acid values increase on depolymerisation whilst the part insoluble in alcohol decreases from 60·6 to 0·5 per cent.[65] Two parts of polymerised shellac are soluble in three parts of phenol. Aliphatic acids such as oleic acid are also suggested as solvents.[66]

The addition of 5 per cent of strong acid to a solvent provides a mixture capable of dissolving polymerised shellac.[67]

Darkening of Shellac Solutions on Storage.—Shellac under certain conditions tends to darken on storage, due to interaction with the metal of the containers. This aspect has been studied by Bhattacharya and Verman, and Gardner and Levy.[68]

The latter investigators demonstrated that the worst darkening occurred with tin, with iron next, and with zinc having the least effect.

The presence of oxalic acid inhibits this discoloration, and earthenware or glass jars are frequently used, instead of metal ones. Sometimes when lacquers formulated on bleached shellacs are applied to oak, darkening may occur. This is attributed by Anderson to the interaction between iron in the shellac and tannin in the wood. Oxalic acid is claimed to prevent this also.[69] Temperature is another contributory cause for the darkening of bleached shellac and the most critical range is recorded as 100°–110° F.[46]

Variation of Drying Time with Age.—The drying time of bleached shellac solutions changes on ageing and this phenomenon has been studied by Zoellner. The drying time is increased more if exposed to diffused light than if stored in darkness. The presence of iron aids in the temporary maintenance of drying properties. Zoellner has devised a method of testing whereby it is possible to predict the drying time of bleached shellac solutions. The reagent used is a solution of thymol blue in aqueous potassium hydroxide. A few drops of shellac solution are added to this reagent and distinctive colours or precipitates are produced. If the precipitate is yellow this corresponds with a drying time of one hour; an ivory precipitate in a chrome yellow solution

corresponds with a drying time of two to three hours; a flesh-coloured precipitate in an orange-red solution corresponds with a time of eighteen hours.[70]

Change of Acidity of Bleached Shellacs on Ageing.—Solutions of bleached shellac tend to lose their acidity on ageing. The important factor appears to be time of storage, although light exerts some influence. Some free acid may be involved in reaction with the metal of the container but reduction of acidity occurs even in the absence of metal.[71]

Deterioration of Bleached Shellac.—Because of the comparatively rapid deterioration of bleached shellac it is used as soon as possible after manufacture. It may be stored under water to prevent deterioration and maintain solubility.

It has been established that the method of manufacture of bleached shellac controls to a substantial degree its keeping properties. Watson and Mulany have given a process whereby shellac is derived which is said to be stable for long periods of time without loss of alcohol solubility. A minimum amount of hypochlorite is used, e.g. one part of bleaching powder to every 6·5 parts of shellac. After precipitation of the bleached product from the alkaline solution by acidification, the excess chlorine is removed from the shellac by shaking with one part of 10 per cent sodium thiosulphate. The product is washed free of soluble matter and dried at ordinary temperatures.[72] Murty, also, has made a comprehensive study of the factors during manufacture which influence the stability of the bleached shellac. His conclusions are not always in agreement with those of other workers, for he states that free chlorine has no effect on the keeping properties. The factors enumerated as follows are said to diminish stability on ageing: too little sodium carbonate in the initial shellac solution, treatment of the lac with mineral acids before dissolving in alkaline solution, rapid addition of hypochlorite, and absolute neutralisation to produce precipitation. Precipitation of shellac by means of an organic acid like acetic acid is preferable to the use of strong mineral acids.[73]

Solvent Retention.—Shellac films show pronounced solvent retention properties. Lubke has reported that alcohol is present in a film of 0·1 mm. thickness, after a year. Nagel and Baumann have confirmed this tendency to alcohol retention.[74]

Water Resistance.—The water resistance of shellac is not of a high order and many attempts have been made to eliminate this defect. The poor water resistance of shellac is attributed to the presence of soft lac resin or the ether soluble part of the resin. Its removal resulting in the production of hard lac resin provides a resin with improved water resistance. The absorption of water by a shellac film causes the film to whiten or bloom. Gardner and Kappenberg have studied the water absorption of shellac films with the following results. When a shellac film is exposed to a moist atmosphere it absorbs moisture rapidly at first, but then slowly loses weight until equilibrium is attained. The

reduction in absorption is believed to be due to swelling of the film.[75] Indiscriminate addition of plasticiser to shellac does not necessarily improve its water resistance. In fact, according to Rangaswami and Aldis the reverse may be the case. The addition of tricresyl phosphate causes an increase in the water absorption.[76] Blooming of shellac films is prevented if they are stoved at 60°–140° C. for one to two hours.[77]

The mechanical strength of shellac is altered substantially according to the conditions prevailing at the time of its assessment. Absorption of moisture from the air softens the shellac by acting as a plasticiser.

Incorporation of Shellac in Drying Oils

Although shellac is used primarily in spirit varnishes, much attention has been devoted to its incorporation in drying oils. In India the utilisation of shellac in oleo-resinous varnishes has reached an advanced stage and large amounts of these varnishes are produced regularly and successfully. Considerable difficulty is likely to be encountered when attempts are made to dissolve shellac directly into drying oils. Temperatures of the order of 380° C. are said to be necessary for the dissolution of shellac in linseed oil, according to Hadert, but the mix must be cooled rapidly to avoid gelling. Large-scale practice has shown, however, that successful results can be obtained at much lower temperatures, and temperatures in the range 250°–280° C. are commonly used. Many solubilising agents have been suggested to facilitate solution at these and lower temperatures ; they include rosin, rosin ester, tritolyl and triphenyl phosphates ; oxides and carbonates of barium and magnesium and carbonates of sodium and potassium ; stearic acid, litharge, and triacetin.[78] Pre-esterification of shellac with monoglycerides produces oil solubility.[79] A similar process can be used for solubilising accroides.

Fielder records the manufacture of varnishes by dissolving shellac in linseed oil monoglycerides. Fresh shellac dissolves readily in monoglycerides at 270°–280° C., if it is added gradually with constant stirring. Alternatively, the shellac may be heated with a mixture of glycerol and high molecular weight unsaturated fatty acids. Fielder believes that the reactions involved include etherification, esterification and polymerisation.[80]

In the experience of the author litharge is one of the best and most convenient of the solubilising agents suggested. The method of incorporation is to dissolve the litharge, previously ground finely in a little of the drying oil, in the drying oil at 240° C. with constant stirring. The temperature of the leaded oil is then maintained at 220°–240° C. and the shellac, broken small, is added in small quantities at a time with constant stirring. Overheating is avoided and as soon as the shellac has dissolved the mixture is cooled and thinned. In a varnish of this type it is an advantage, although not absolutely essential, to use thinners with strong solvent power. Thus a mixture of white spirit and naphtha

may be used, and it is sometimes convenient to include a percentage of butyl alcohol also. Other drying soaps, especially those of manganese, greatly facilitate the dissolution of shellac in vegetable oils. Shellac-drying oil compositions show a tendency to instability on storage. Aldis has incorporated castor oil with shellac at 270° C. If glycol is present the temperature of incorporation may be reduced.[81] By adding a shellac which has become insoluble in alcohol to 1½ parts of rosin at 270° C. a product is obtained which is soluble both in drying oils and aromatic hydrocarbons.[82] Bhattacharya has discussed the subject of oil solubility of shellac fully in a recent paper.[83] Shellac dissolves more easily in boiled oil if it is previously treated by boiling with red lead dispersed in water.[90]

Uses

Shellac is a raw material with valuable properties which meet the requirements of many industries. A comprehensive list of its uses would include the manufacture of french and white polishes, foil lacquers, lacquers for wood and metal, media for white road paints and anti-fouling paints, hat stiffening lacquers, cellulose lacquers, good quality sealing waxes, gramophone records, water varnishes for leather and paper, varnishes for rubber, media for mirror backing paints, adhesives and cements for wood, paper and metal; lacquers for cans, painting compounds for oil tanks, gaskets, etc.; sealing primers, seaming solutions for cans, glazing of confectionery, lacquers for playing cards, and lacquers for shells, fuses and detonators to many government specifications.

One of the most important consumers of shellac is the electrical industry. Shellac has good insulating properties, and is not susceptible to tracking. Pure shellacs only should be used in insulating compositions and they should be free of orpiment and rosin. Shellacs are used in the production of moulded electrical components; in micanite from mica dust, for wire enamels, for laminated paper tubes, and for impregnating and finishing varnishes for coils, cotton and paper.

The soft lac resin produced in the manufacture of hard lac resin can be used in varnishes. This is rendered possible by condensing it with aniline and formaldehyde, phenol and formaldehyde, or with acetone and phosphoric acid.[84]

A method of hot spraying of shellac has been devised.[85]

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Sandarac

Sandarac is an exudation of coniferae which occur in North and South Africa and Australia. The tree yielding sandarac is found also in North America. Other sources of the resin are Tasmania and the West Indies. North African sandarac is called Mogador sandarac. Sandarac is also known as pine resin or gum juniper. The exudation of the resin may be hastened by incision. The resin appears on the market in the form of drops or tears which have a pale yellow colour. It may be contaminated with dust and dirt but the resin commands a high price and normally it is almost free of dirt.

According to Balzer the resin is composed almost entirely of a mixture of two carboxylic acids, namely sandaracolic and callitrolic acids.[1] Sandarac has an acid value of 140 approximately.

Sandarac should be examined for initial colour, colour in solution, clarity of solution, viscosity of solution, and percentage of insoluble matter.

Sandarac is a harder resin than mastic and powders fairly easily. It has a characteristic smell and a melting-point of 150° C. It yields brittle films and like other spirit soluble resins, such as Manila, it needs

plasticising. Barry and Dunster suggest camphor, Venice turpentine, and elemi as suitable plasticisers.[2]

It is soluble in alcohols, turpentine, ether, and acetone, and partly soluble in chloroform, carbon disulphide, white spirit and petroleum ether. It is insoluble in benzol and esters.

Its uses include the manufacture of paper varnishes used for labels, maps, etc.; varnishes for bookbinders, lacquers for leather and metal, blackboard varnishes and negative varnishes.

Mastic

Mastic comes from Greece, the Grecian Islands especially Chios, North Africa and Central Asia. It is an exudation caused by incision and is available in the form of pale yellow tears.

It is a softer resin than sandarac, having a melting-point of 105° C. approximately. It has a tendency to brittleness. Its acid value is about 50–55. Mastic is said to be more durable than damar.

Mastic is soluble in turpentine, chloroform, acetone, alcohols, carbon disulphide, esters and aromatic hydrocarbons. The solubility in petroleum hydrocarbons varies with the type of resin. The solubility is given in literature as soluble, partly soluble or insoluble in petroleum hydrocarbons.

Mastic is the basic constituent of varnishes for pictures, maps and of artists' paint media.

Blends of mastic may be made with damar or sandarac.

Acroides

Gum accroides is known by many different names, including acaroid resin, grass tree gum, yacca gum, black boy gum, and xanthorrhoea resin.

Two varieties of the resin are known; yellow and the red variety. The yellow variety is sometimes described as Botany Bay gum, and the red as red gum accroides.

The resin is obtained from *Xanthorrhoea Australis*, *X. hastilis*, *X. arborea*, *X. quadrangularis*, *X. Drummondii*, and *X. Preisii*. The places of origin include Australia, New South Wales, Tasmania and Kangaroo Island.

The resin is obtained as an exudation. Semi-fossilised resin is also found sometimes.

Accroides as it reaches the consumer is usually in a very dirty condition. It contains dirt and substantial quantities of wood, bark, etc. This may constitute as much as 10 per cent of the total weight of the resin.

The red resin consists chiefly of the erythroresinotannol ester of paracoumaric acid. Small amounts of paracoumaric acid and paraoxybenzaldehyde are also present.[3] Yellow accroides consists chiefly of the xanthoresinotannol ester of paracoumaric acid. Free paracoumaric and cinnamic acids are present also.[4]

Apart from the difference in colour the presence of cinnamic acid distinguishes the yellow resin from the red.

Both resins are examined for percentage soluble in alcohol. It is very difficult to cleanse the solutions of extraneous matter, and the only really satisfactory way is to remove the large insoluble matter by rough straining and to pass the remainder through a centrifuge. This will not remove the very fine dirt, but the condition of the solution may be such as to permit its use for certain purposes. If more bit-free solutions are desired it is best to allow the solutions to stand and settle. The clear supernatant liquor is then removed. Attempts to filter press these solutions often result in rapid clogging of the papers.

Yellow accroides has a melting-point of 97° C. compared with 110° C. for the red resin.

The resins are soluble in alcohol, but insoluble in aliphatic and aromatic hydrocarbons. The resins are only partly soluble both in chloroform and ether. Like shellac the resins are soluble in alkali. They are not very resistant to water and darken on stoving. They have poor durability.

Accroides resins are used in yellow and red spirit stains, in which the natural colours of the resins are exploited. The red resin especially may form the basis of cheap black air-drying lacquers involving the use of black pigment or dye. Their insolubility in hydrocarbons suggests their incorporation in petrol-resisting lacquers. They may be used instead of rosin for sizing paper and for sealing wax. They are sometimes used in cheap metal lacquers.

Benzoin

Benzoin, which has been described as a resin, gum or balsam, is not of very great importance to the spirit varnish manufacturer. Several different types of benzoin are available. Siam benzoin obtained from styrax benzoin of Siam is generally regarded as the best type. Other types are Palembang, Padang, Sumatra, and Penang benzoins. Sumatra benzoin, like Siam benzoin is obtained from styrax benzoin in Sumatra. Penang benzoin is believed to be obtained from styrax subdenticulata of Farther India. The origins of Palembang benzoin and Padang benzoin are uncertain.

Palembang benzoin is the next grade to Siam, with Sumatra as the inferior of these two. The constituents of benzoins have been given by Lüdy.[5] Benzoin is an exudation obtained on incision. It is a soft resin, melting below 100° C. Siam benzoin may be obtained in the form of very pale tears or as a mixture of white and yellow resinous matter. Sumatra benzoin is a darker mixture consisting of pale and reddish-grey matter.

Benzoin resins are soluble in alcohol, but only partly soluble in hydrocarbons. They have a distinct " vanilla " smell.

Benzoin resins normally contain substantial amounts of dirt and the precise amount present should be determined in each consignment before use.

Benzoin is used in spirit varnishes to give the resulting films a pleasant aroma and it also acts as a glossy softening agent.

Elemi

Elemi is obtained from Icica Icicariba, Amyris Plumieri and Canarium commune. The resin is collected in the Philippines (Manila), West and East Indies, South America, Central America and Africa. The elemi from the Philippines is known as Manila elemi; from America as Rio, Mexican, Vera Cruz or Brazilian Almessega elemi; from the East Indies as East Indian elemi, and from Africa as Luban Matti elemi.

Elemi resins may be subdivided further into two grades, soft and hard. Bulungu resin from the Belgian Congo is stated by Stock to be similar to elemi. Because of the fact that it chars on heating and by reason of its insolubility in linseed oil it is not a satisfactory varnish resin.[6]

According to Dieterich, fresh elemi is a solution of resins in an ethereal oil. Part of the resins may be in crystalline form. The crystalline deposition explains the turbidity of the resin. Phellandrene and dipentene are obtained by distilling elemi.[7]

Lieb and Mladenovic have examined the constitution of Manila elemi.[8]

The colour of elemi varies, depending on its source, from white, through golden-yellow to greyish-black. The white grades are Manila and Yucatan elemi.

The smell of elemi is characteristic and is said by some to be of a terpenic nature. Others have stated that it is reminiscent of lemons.

Its acidity varies from 1·2 to 39·4, depending upon the source of the resin.

Elemi is soluble in alcohols, ether, benzol, acetone, turpentine, petroleum hydrocarbons, chloroform and carbon disulphide. Solubility in petroleum hydrocarbons is apt to be variable.

Elemi deteriorates on exposure.

Its most important uses are as a plasticiser for spirit varnishes and as a plasticising resin for nitrocellulose lacquers or enamels, particularly of the brushing type.

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Gum Thus

Gum thus is the oleoresin which exudes from the rosin-producing trees and which adheres to the tree and hardens. Gum thus is sometimes

known as "scrape" and it contains less volatile matter (turpentine) than the original oleoresin.

Gum thus is not used to any appreciable extent in the manufacture of modern varnishes. Its chief use is in spirit varnishes where it performs the function of a plasticiser.

Venice Turpentine

Source.—Venice turpentine is an exudation of the larch tree (*Pinus larix, Larix decidua*). The sources of Venice turpentine are the Tyrol and Piedmont although larch forests occur also in Poland.

Production.—The oleoresin is not obtained by incision but by drilling into the heart wood. It is a clear pale greenish-yellow viscous liquid.

Composition.—According to Morrell it consists of resin acids (60–64 per cent), essential oils (20–22 per cent), resenes (14–15 per cent) and other constituents (2–4 per cent).[1] Dieterich gives the constituents as caffeic acid, ferulaic acid ?, abietic acid, formic acid, vanillin, ethereal oil, bitter principle and water.[2] Schmied gives the composition as laricinolic and larinolic acids and laricoresene.[3]

Properties

The acid value of Venice turpentine varies from 65 to 100. Schmied gives 70 as an average figure. It is soluble in petroleum and aromatic hydrocarbons, alcohols, ether, acetone, chloroform and turpentine. By steam distillation a turpentine can be obtained from Venice turpentine which resinifies on exposure to air.

Artificial Venice turpentines have been made and consist chiefly of mixtures of rosin, rosin oil and turpentine.[4]

Uses

The chief function of Venice turpentine is as a plasticiser in spirit and other varnishes. Venice turpentine is also used in the manufacture of sizes for fabrics, in sealing wax, in cements, and in artists' colours.

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Zein

Zein is included among the natural spirit varnish resins, not because of its resinous characteristics, but because of its solubility in industrial alcohol and the fact that it can substitute the well-known spirit soluble resins in certain formulations.

Chemically it is a protein, extracted from maize, or the gluten, thereof, by means of isopropyl alcohol.

Its films have properties intermediate between those of shellac and casein. It is less water-resistant than shellac—it is, in fact, soluble in alcohol-water mixtures—but more water-resistant than casein.

In combination with rosin in alcohol, oil resistant lacquers are obtained. In Canada and the U.S.A. large amounts have been used in protective lacquers for paper, and these products are still in the process of successful development.

Zein is soluble in ethyl alcohol, benzyl alcohol, diacetone alcohol, cellosolve, and glycols.

A typical lacquer for grease-proofing paper, etc., contains zein, 100 ; ethyl alcohol (92 per cent), 300 ; urea, 12 to 20 ; and propylene glycol, ethylene glycol, or di- or tri-ethylene glycol, 12–30 parts.[1]

The flexibility and water resistance of zein can be improved by acetylation.

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CHAPTER 6

MODIFIED NATURAL RESINS

Ester Gum

Ester gum or rosin ester as it is sometimes called is really the triglyceride derived from rosin. Rosin or its constituent acids, however, has been reacted with a large number of alcohols or hydroxy compounds with the formation of esters. With the passage of time profound modifications have been made in common rosin, and these modified rosins, naturally, have been converted into esters with suitable alcohols. Esters of hydrogenated, dehydrogenated and polymerised rosin have been made commercially, and are in the process of assessment.

Alcohols used for Esterification of Rosin.—Rosin has been reacted with monohydric alcohols such as methyl, ethyl, *n* and isopropyl, *n* and isobutyl, amyl, allyl, benzyl, cholesteryl, menthyl, bornyl, stearyl, ceryl, myricyl, cetyl and cyclohexyl alcohols; and polyhydric alcohols such as glycerol, polyglycerols (diglycerol), ethylene, diethylene, and butylene glycols, pentaerythritol, dipentaerythritol, erythritol, mannitol, dulcitol and sorbitol.

Other Esterifying Agents.—Other esterifying agents used include phenol, cresol, naphthol, tetrahydronaphthol, resorcinol, acetins, monobutyl ether of diethylene glycol, chlorhydrins, bromohydrins, alkylene oxides, chloroethers, benzyl, methyl benzyl, dimethylbenzyl, isopropyl benzyl, benzal, tolyl, and xylyl chlorides, and many esters.

Esterification Methods

Direct Interaction between Rosin and Alcohol.—Many different methods may be used to effect esterification of rosin. Rosin is heated with a slight excess of glycerol. The rosin may be melted, the glycerol added and the heating continued until the best reaction temperature is reached, and this is maintained until the reaction is complete. Alternatively the rosin is heated to the reaction temperature and the glycerol introduced under the surface of the hot rosin. The reaction temperature is maintained as before.

The reaction is facilitated by removal of the water evolved and this may be accomplished by using a slight vacuum, passing hot neutral gases through the reaction mixture,[1] or by adding compounds like acids which are capable of absorbing water. The plant may be fitted with a condenser designed to condense glycerol but which allows a free exit for the water vapour. Esters of monohydric alcohols are obtained by refluxing the alcohol and rosin together. This may be accomplished under pressure, in which case, higher reaction temperatures are possible. Thus, rosin and ethyl alcohol are heated at 160° C. and 11–12 atmosphere

pressure for four hours in the presence of *p*-toluenesulphonic acid to yield ethyl abietate. Using oleum as a condensing agent, rosin and ethyl alcohol can be refluxed at ordinary pressure to yield the abietate.[2]

Another method of obtaining a rosin ester is to prepare a solution of the rosin in the alcohol and to pass the solution through the reaction vessel at a high temperature and under pressure.[3]

Ester Interchange.—Apart from the direct interaction of rosin and alcohol, esters of rosin may be obtained by a variety of other means. If a high temperature can be attained ester interchange can be induced between esters and rosin to yield rosin esters. Thus rosin can be heated at temperatures of the order of 290° C. with esters such as dimethyl, diethyl, and dibutyl phthalates, or glyceryl tristearate.[4] In place of normal esters rosin may be heated with partial esters such as mono and diacetin.

Other Methods.—By a laborious process rosin ester can be obtained from the interaction between rosin and the monobutyl ether of diethylene glycol. Between thirty and seventy hours at 200°–220° C. are necessary for the reaction.[5] A rosin ester is obtained by heating rosin and ethylene oxide at 160°–170° C. under pressure.[6] A glycol ester of rosin is obtained by heating a solution of caustic soda, alcohol, rosin, and $\beta\beta'$-dichloroethyl ether at 160° C. under pressure for eight hours.[7]

Ethyl abietate is made by adding diethyl sulphate to an aqueous alcoholic solution of sodium resinate and heating.[8]

When rosin, benzyl chloride, with zinc chloride as catalyst, are heated together first at 100° C. to remove hydrochloric acid and finally at 200° C., a rosin ester results.[9] Or sodium resinate can be refluxed with benzyl chloride to yield a resin.[10]

Rosin can be reacted directly with phenols to yield phenolic esters. Rosin and phenol are heated together at 280° C. and ten atmospheres pressure in the presence of a catalyst such as zinc chloride. Rosin esters are derived from the interaction of calcium salts of phenols and rosin at 180°–220° C.[11]

Reaction between Rosin and Glycerol

Although the foregoing represents a fairly complete survey of the reactions which are possible for the formation of esters from rosin, it is the direct interaction between glycerol and rosin which is by far the most important from the varnish maker's point of view.

Temperature.—The speed of the reaction is controlled largely by the temperature used. Reaction occurs between rosin and glycerol at relatively low temperatures (150° C.), but much higher temperatures are necessary to make the reaction proceed at an economical rate or to effect complete esterification.[12]

Using rosin (105·3 pts.), of acid value 160, and glycerol (9·2 pts.) the author noted a reduction in acid value to 50 after six hours at 260° C. The mixture gave a clear bead on cooling after two hours at 260° C. When the reaction temperature was raised to the boiling-point of

glycerol (290° C.) esterification was completed in fifteen minutes when the reactants were rosin (100 pts.) and glycerol (12 pts.).[12] 280° C. has been suggested as the best temperature for esterification of rosin (100 pts.) with glycerol (12 pts.), and three hours treatment is required. If the heating of rosin ester is continued too long decomposition of the ester may occur, resulting in liberation of free acid. If rosin is esterified with alcohols other than glycerol the reaction temperature needs modification. With a mixture of rosin (90 pts.) and ethylene glycol (10 pts.) Borgmann uses a temperature of 230°–235° C. in an autoclave. Other workers suggest that rosin (100 pts.) and ethylene glycol (13 pts.) are heated slowly from 180°–280° C.[13] Rosin esters are prepared from ethylene and propylene glycol in two stages. The rosin is first heated with about half the equivalent amount of alcohol at 250°–290° C. The remainder of the alcohol is then added slowly while the temperature is maintained.[47] Diethylene glycol (20 pts.) and rosin (100 pts.) are heated together for a total time of fifteen hours at 250°–260° C., using a catalyst. An ester gum is obtained from rosin and butylene glycol by refluxing at 245° C. for several hours.

Rosin is esterified with stearyl alcohol by heating at 200° C. for several hours. The final product is described as a soft resin.[15]

Pressure.—As indicated already, the high reaction temperatures for monohydric alcohols and rosin may be attained by increasing the pressure, and another example for the production of ethyl abietate from ethyl alcohol and rosin uses a temperature of 265° C. and a pressure of 800 lb. per square inch.[16]

The use of pressure in the reaction between rosin and glycerol does not offer any very great advantages, although the reaction at 250° C. and several atmospheres pressure has been recorded. The use of reduced pressure, however, offers greater possibilities. Some processes use reduced pressure to aid in the removal of the water eliminated, but there is also the danger of simultaneous removal of glycerol. The application of a vacuum at the conclusion of the reaction to remove the last traces of water or unreacted glycerol is a distinct advantage.[17] The removal of free glycerol from ester gum is important for to its presence is attributed the two defects of inferior water resistance and the blooming of dried varnish films.

Amount of Glycerol.—Since, normally, the reaction between rosin and glycerol is conducted at temperatures near or at the boiling-point of glycerol, the loss of this reactant is often appreciable. The extent of the loss is exaggerated also by means adopted for water removal. It is, therefore, the usual practice to use an excess of glycerol to counterbalance any losses. An excess of 2–5 per cent of glycerol calculated on the rosin present, above that required theoretically, is the quantity generally recommended.

An increase in the amount of glycerol greatly accelerates the reaction and enables products of lower acid value to be obtained. Thus rosin

(105·3 pts.) and glycerin (9·2 pts.) gave a product with an acid value of 50 after six hours at 260° C. When the glycerol was increased to 11·5 parts the acid value dropped to 22 after similar treatment. It was noted that whereas using the smaller quantity of glycerol the reaction product was clear on cooling after two hours at 260° C., with the larger quantity four hours' treatment was necessary.

Catalysts.—Many catalysts have been suggested to facilitate the esterification of rosin with glycerol and these include: oxides of zinc, lead, calcium, barium, and magnesium,[18] metals such as zinc, cadmium, aluminium, magnesium, copper, cobalt, steel,[19] metallic salts, including resinates of calcium, cadmium and lithium; chlorides of iron and zinc, zinc carbonate, calcium cyanamide, sodium acetate,[20] and acids such as hydrochloric, carbonic, sulphuric, orthophosphoric, orthophosphorous, diglycollic,[21] boric, *p*-toluene sulphonic, succinic, and oleum.[2] Drying oils are also stated to have a marked catalytic effect on the esterification, and of these tung oil has the greatest effect, which may be improved still further by the addition of organic calcium salts.[22]

(*a*) *Calcium Oxide.*—Experiments conducted on the esterification of rosin with glycerol in the presence of calcium oxide gave the following results:—

Using rosin (105·3), glycerol (11·5) and calcium oxide (0·117) the acid value was reduced to 6·5 in ten hours at 260° C. In the absence of calcium oxide under the same conditions the acid value was reduced to 12·3 only. If the glycerol in the first experiment, using calcium oxide, is reduced to 10·3 the acid value falls to 8·0 in ten hours at 260° C.; if the glycerol is reduced to 9·76 the final acid value is 13·5. A more rapid process for the production of ester gum involves the use of much larger amounts of catalyst. Thus rosin (300 pts.) and calcium oxide (12 pts.) are first reacted at 290° C. for thirty minutes, after which glycerol (40 pts.) is added and the reaction continued at 270°–290° C. for a further thirty minutes. The resultant resin had an acid value of 9·0.[21]

(*b*) *Zinc Oxide.*—Zinc oxide was found to be a very efficient catalyst and better than calcium oxide. Rosin (105·3 pts.), glycerol (11·5 pts.) and zinc oxide (0·117 pts.) gave an ester with an acid value of 10·4 after four hours at 260° C. With the glycerol reduced to 9·76 parts an acid value of 19·1 was obtained after four hours.

(*c*) *Litharge.*—Using rosin (105·3 pts.), glycerol (9·76 pts.) and litharge (0·117 pt.) an acid value of 28·0 was attained after four hours at 260° C. and had diminished to 16·4 after ten hours' treatment.

(*d*) *Sulphuric and Hydrochloric Acids.*—In using strong or concentrated sulphuric acid as catalyst great care must be exercised to avoid the reaction getting beyond control. The acid should be added slowly at the minimum temperature possible to avoid excessive frothing. Hydrochloric acid may be bubbled through in the gaseous form. Rosin (100 pts.) and glycerol (10–16 pts.) were heated together at 285° C. for two hours whilst hydrogen chloride was bubbled through. The acid value of the ester obtained was 11·0 approximately.[21]

Although the use of catalysts undoubtedly facilitates the esterification of rosin it is not the general practice to use them, for the consumer does not regard ester gums containing zinc or calcium with favour.

Reduction of Free Acidity.—The free acidity remaining after the normal esterification process may be reduced by the addition of basic oxides such as zinc oxide or calcium oxide, but this practice is not recommended for it is commonly held that durability is affected.

Effect of Metals.—The catalytic effect of metals upon esterification is an important point in manufacture, for it may influence the choice of plant. Iron acts as a catalyst but gives ester gums of inferior colour. Aluminium vessels are popular. The metal not only acts catalytically but enables pale products to be produced also. There is some element of danger in using glycerol in aluminium vessels at high temperatures and this aspect should be borne in mind. Stainless steel can be used for the reaction vessel but little information is available of its catalytic effect.

Agitation.—Due to the high specific gravity of glycerol, there is a strong tendency for it to settle to the bottom of the reaction vessel. Convection currents are not normally strong enough to provide adequate stirring and continuous agitation by means of a mechanical stirrer is a distinct advantage. Apart from choice of metal for the reaction vessel, paleness of colour is preserved in the reaction product by stirring and by conducting the esterification in an inert atmosphere like carbon dioxide or nitrogen.

In esterifying glycols it is reported that the presence of higher homologues greatly facilitates the reaction. Thus a glycol containing 40 per cent. higher homologues behaves better than pure glycol.[13]

Purification.—After the esterification, ester gums are not usually subjected to any other treatment before sale, unless it be to remove all traces of water and excess glycerol. Processes have been described, however, designed to improve the colour of ester gum. Treatment of ester gum with phenol or resorcinol is stated to be effective in removing colour, or a solution of rosin ester is treated with furfuryl alcohol or furfural.[23] Fractions of varying hardness may be obtained from the original ester by vacuum distillation.[24]

Composition.—The composition of the ester gum of commerce is somewhat complex. Although the primary object of the manufacturer is to produce a compound approximating close to glyceryl triabietate other impurities may be present, including the mono and diabietates, the non-acidic compounds in the original rosin, traces of free glycerol and possibly some catalyst. The mono and diabietates may be detected by their water solubility.

The conditions of esterification used with rosin and glycerol are such that some of the glycerol is sure to be involved in a side reaction to produce diglycerol, with elimination of water. The diglycerol, in turn, reacts with any available rosin, and esters of diglycerol are thus present in ordinary ester gum. The diglycerol ester is reconverted partially into

the triabietate if it is heated with an excess of rosin. According to Woodruff (*loc. cit.*) it is possible to separate chemically pure glyceryl triabietate from the diglycerol-rosin ester, in that the former is insoluble in Varnolene and ethyl acetate, whereas the latter is not.

The presence of free glycerol in ester gum lowers the water resistance, but if glycerol is replaced by polyglycerol during esterification, any unreacted alcohol has no such harmful effect.[25]

Testing

Ester gum is tested for colour, acid value, solubility in white spirit and cellulose solvents, solubility in oil, melting-point, tendency to crystallise from solution, and ash.

Properties

Ester gum has an acid value varying from 6 to 10 and a melting-point of 85° C. approximately, although resins with melting-points as low as 53° C. are obtainable.

The higher the melting-point, the harder the resin and the resulting film, and the better the drying properties. Ester gum is soluble in aliphatic and aromatic hydrocarbons, vegetable oils, turpentine, ether, acetone and in many cellulose solvents. According to Hofmann ester gum is insoluble in Cellosolve, Cellosolve acetate, diacetone alcohol and ethyl lactate.[26]

Ester gum differs from rosin in its solubility in alcohol. Most grades of ester gum are almost completely insoluble. So-called alcohol soluble ester gums are available, but these are highly acidic resins and bear little resemblance to true ester gums which are almost neutral.

Like rosin some ester gums have a tendency to crystallise from solution and this tendency should be tested. If solutions of ester gum are made in esters the addition of substantial quantities of aromatic hydrocarbons is sometimes necessary to prevent crystallisation on storage.

The solubility of ester gum may change on storage, especially if it is in the form of very small lumps or powder. This change in solubility is attributed to surface oxidation. According to Saphier oxidation during storage explains why powdered ester gum frequently gives darker varnishes than lump resin.[27]

The low acidity of ester gum permits its use in paint and enamel media which have to be used with basic pigments. Its low acidity makes the preparation of satisfactory wood oil varnishes difficult, although straight ester gum-wood oil varnishes are made. Ester gum exerts practically no influence on the time necessary for gelation of wood oil except in so far as it acts as a diluent. Huff records, however, that as the free acidity of ester gum increases the retardation of gelation becomes more pronounced.[28] This is easy to appreciate when the peptising action of rosin on polymerised wood oil is recalled. Ester gums do not possess outstanding durability, and films containing them, unless they are very rich in wood oil, tend to exhibit a degree of surface tackiness.

Like rosin, ester gums permit the production of very pale varnishes and media, and they are very compatible with most other common varnish-making raw materials. Ester gum has better alkali resistance than rosin.

When glycerol is replaced by other alcohols the resulting esters vary considerably in properties. Thus most of the esters from rosin and monohydric alcohols are liquids of different viscosities. Of these, the most important are methyl, ethyl and benzyl abietates. Methyl abietate is a pale yellow liquid resin, with a boiling-point of 225° C./16 mm. It has an acidity of 5 per cent approximately, calculated as abietic acid. It is soluble in most organic solvents and has good compatibility with most varnish-making raw materials. Ethyl abietate has similar properties to methyl abietate. It is a pale yellow liquid resin with a boiling-point of 350° C., approximately, at ordinary pressures, or 205° C./4 mm. Its solubility and compatibility are good and resemble those of methyl abietate. Durrans records that the ester has a tendency to darken on exposure and to become brittle.[29] Benzyl abietate is a soft solid with good solubility. It has a boiling-point of 295° C./4 mm. The ester from butylene glycol is a sticky but brittle resin.

Crebert has studied the influence of higher alcohols than glycerol on the properties of the ester gums obtained. As the number of hydroxyl groups in the alcohol increases the corresponding ester gum increases in melting-point and solubility changes occur. Glycerol is considered inferior to polyhydric alcohols containing more hydroxyl groups, as a resin component. Esters from erythritol, mannitol, dulcitol and sorbitol are all considered superior to the ester from glycerol. The pentaerythritol ester has poor colour if made from ordinary commercial pentaerythritol. It has good oil compatibility, and acid values of the order of 12 can be obtained. This ester is claimed to improve the water resistance and durability of oil varnishes.[30] The alkali resistance of the pentaerythritol ester is superior to that of the glyceryl ester.

Uses

Ester gum is widely used in the varnish trade. It may be used alone or in conjunction with copal ester, in paint and enamel media where acid value is of primary importance.

Enamels based on ester gum media do not stand up well under tropical conditions involving high humidities and temperatures. Films tend to remain sticky for long periods and ultimately chalk. The durability of ester gum varnishes can be improved, however, by the addition of 0·1 per cent. of sulphur.[31]

The low acidity of ester gum also makes it a popular choice for media for metallic paints, especially when used with wood oil, or in insulating varnishes for impregnation of coils or fabric where films of low acidity are important. Wood oil varnishes containing ester gum, sometimes reinforced with better grade resins, are used as boat varnishes. With the introduction of pure phenolic resin, ester gum has assumed some

importance as a diluent. Experiments have shown that substantial amounts of ester gum can be added to pure phenolic resins without seriously affecting the properties of the finished varnish. The introduction of some pure phenolic resin to ester gum varnishes based on wood oil has the important result of enabling varnishes free from webbing tendencies to be produced. The alcohol soluble ester gum has been used in spirit varnish media for the production of white road line paints due to temporary scarcity of spirit Manila. Ester gum is also used in considerable quantities in cellulose lacquers to impart gloss, hardness, and to increase the solid content.

Other uses for ester gum include media for antifouling paints, stoving varnishes for tin-plate, cementing compositions for the manufacture of linoleum, printing inks, and in conjunction with waxes for impregnating waterproofing compositions for paper and fabric.

Stearyl abietate is used in shoe polishes.[32] The ethylene glycol ester of rosin in alcoholic solution is said to be used for polishing wood.

Polymerised Ester Gum.—Many modifications of ester gum have been made although they have not, as yet, assumed any great importance.

Under certain conditions, ester gum can be polymerised. This is accomplished by dissolving the resin in a solvent and subjecting the solution to the action of ultra-violet light, sulphuric acid, zinc chloride or tin tetrachloride.[33]

Alternatively a polymerised ester gum can be made by starting with polymerised rosin. A polymerised rosin ester of this type is superior to the unpolymerised ester, in hardness, colour, and stability, and possesses a lesser tendency to crystallise from solution. Polymerised rosin esters are more economical in manufacture since they require about 10 per cent less glycerine for a product of convenient low acidity.

Oxidised Ester Gum.—The melting-point of ester gum can be raised by oxidising it by means of air. The resin, after powdering, is spread out in thin layers at 50°–80° C. and the oxidation process takes several days.[34]

Hydrogenated Ester Gum.—Hydrogenation products have attracted more attention than oxidation ester gum products. The chief object of hydrogenated ester gums is to provide resins with diminished yellowing tendency. Thus methyl abietate is hydrogenated under a pressure of 10–500 atmospheres at 140°–250° C. in the presence of a catalyst. A resin similar to methyl tetrahydroabietate is obtained. Molten ester gum is hydrogenated similarly in the presence of a catalyst.[35]

According to Ellis the best method for hydrogenating ester gum is in the presence of a solvent, using an activated acid and a catalyst. The solvents suggested are aromatic and aliphatic hydrocarbons, esters and alcohols. The activating acids are hydrochloric, acetic, formic and phosphoric, and the catalysts are the usual hydrogenation catalysts such as platinum, palladium, nickel and chromites of nickel, copper and zinc.[36]

The alternative method of producing hydrogenated ester gum is to commence with hydrogenated rosin which is esterified with glycerol.[37]

Copal-Rosin Esters.—Mixed copal-rosin esters are also produced and these are generally harder than rosin ester, with higher melting-points. They are also usually appreciably darker in colour.

Natural copals are more difficult to esterify with glycerol than rosin, hence the introduction of rosin during the esterification greatly facilitates it.

The Congo is dissolved in the rosin at temperatures above 300° C., the mixture cooled, glycerin is added and esterification is effected at 288° C. Another process describes esterification of the mixture at 270°–290° C. and records that the reaction is assisted by the presence of calcium resinate.[38]

Other Modified Ester Gums. (*a*) *Involving Glycerol.*—Further modifications of ester gum consist in esterifying rosin with glycerol in the presence of phthalic anhydride.[39] Regarded from another angle the resin formed is really a rosin modified alkyd. Another type of alkyd resin is obtained by reacting together hydrogenated rosin, drying oil fatty acids, phthalic acid and glycerol.[40] Glycerol, linseed oil fatty acids and rosin are also reacted together to yield a modified ester gum.[41] The melting-point of ester gum can be increased by treatment with boron trifluoride. Acid value and iodine value are reduced simultaneously.[42] An oil soluble resin is obtained by condensing rosin and an aldehyde together in the presence of a catalyst and esterifying the reaction product with glycerol.[43]

(*b*) *Involving Other Alcohols.*—Other products which bear some similarity to abietic acid esters are those derived from abietyl alcohol or the hydrogenated alcohol. Resins are made by condensing these alcohols with polybasic carboxylic acids which may be aliphatic or aromatic dibasic acids or the reaction product of rosin and maleic anhydride. Acidic substances aid the condensation and include zinc chloride, sodium bisulphite, boric and *p*-toluene sulphonic acids. Other acids stated to be suitable for esterifying hydrogenated abietyl alcohol include the following: acetic, palmitic, ricinoleic, tartaric, citric and benzoic acids.[44]

Much research work has been conducted on the esterification of rosin and modified rosins with polyalcohols other than glycerol. A very useful summary of this work, with information on the properties of the resultant resins, has been given by Woodruff.[46]

The melting-points of the various esters increase with the hydroxyl content of the polyalcohol used for esterification. The glycol ester is a semi-liquid product; the glycerol ester has a melting-point of about 94° C., the pentaerythritol ester about 105° C., and the mannitol ester about 110° C. Considering the wide divergencies in the number of reactive centres, these comparatively slight differences are disappointing to the formulator. In solution, the differences in the resultant viscosities are even less marked. On the whole, therefore, the rosin esters of the more complex alcohols do not offer any great advantages over the old established and well-tried glycerol ester.

Varnish Constituents

More success has been obtained with the ethylene glycol and pentaerythritol esters of polymerised rosin. The ethylene glycol ester has a melting-point of 75° C. which is similar to that of the glyceryl ester of wood rosin. Its chief application is in nitrocellulose lacquers because it is rather too soft as an oil varnish resin. The pentaerythritol polymerised rosin esters are much more interesting generally. They are appreciably harder and more reactive than the natural or wood rosin esters.

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Copal Ester

Copal ester, although in many respects a superior resin to rosin ester, has not attracted the attention which the latter has, and it is not used in such large quantities. The reasons for this difference of popularity may be because of the increased difficulty of esterification of copal, the higher resultant acidity, the inferior colour and the higher price.

Esterification of Natural Copals

During the esterification of rosin with glycerol there is no tendency for gelation. The opposite occurs with copals and these need careful heat treatment before the glycerol is added. Ellis gives an example of this phenomenon wherein Congo was run at 327° C. until it was soluble in turpentine. On the addition of glycerol a vigorous reaction occurred and the whole mass gelled.[1] The tendency to gel on addition of glycerol was confirmed by Gardner and Holdt.[2] Hellinckx found that Congo, run until its acid value had been reduced to 70 per cent. of its original figure, gelled when esterification with glycerol was attempted.[3] Other natural copals which exhibit the same tendency to gelation on esterification are Pontianac and Manila. Copal esters are available from Kauri copal.

This gelling tendency is overcome if the natural copal is run sufficiently before esterification. Gardner and Holdt stipulate that the copal should be run at 280° C. or higher for a minimum of seventy minutes, depending upon the type of plant used. A running temperature of 315°–325° C. is given as most satisfactory, and before adding the glycerol (6–8 per cent) the run gum is cooled to 280° C. The esterification reaction is conducted at 292°–295° C. A method worked out by Ellis uses a similar temperature range for running the gum but extends the treatment to 3½ hours, after which glycerol is added (1/16th weight of gum) and esterification is conducted at 300° C.[4] Hellinckx states that satisfactory esterification of Congo with glycerol is possible only when all the dibasic acids present initially in the copal are disintegrated into monobasic acid by running.[3] The monobasic acids permit esterification without gelation.

According to Gardner and Holdt, using a run copal with an acid value of 80, and 6 per cent of glycerol, a copal ester of acid value 5·5 is obtained after two hours' treatment at 280° C. Billing states that esterification of copal is commonly conducted when the acidity has been reduced to about 67.[10]

Like the reaction between rosin and glycerol, that with copals is facilitated by using excess glycerol or catalysts.

Instead of using run copals the natural copal can be prepared in a condition suitable for esterification by mastication over heated rollers.[5]

Esterification in the Presence of Oil.—Another method of preparing copal esters is to run the copal in the usual way and to oil down with linseed

oil. The temperature is maintained at 280°–290° C., and glycerol is added. The reduction of acidity can be followed by withdrawing samples and determining the acid value in the usual way. By this means, from a graph, it is possible to estimate the duration of treatment necessary to obtain a medium with a conveniently low acid value.

Copal esters may be obtained by heating copal with high boiling esters, and this method has the advantage that the running process is eliminated. Thus Congo and stearic triglyceride are reacted together at 300° C. for four hours. The stearic acid eliminated by the reaction is removed by distillation under vacuum. A copal ester is obtained possessing the exceptionally low acid value of 1·5.[6]

Copals may be esterified with various phenols to yield useful resins if desired.[7]

Properties

Copal esters are harder resins than the corresponding rosin esters and have higher melting-points. They are, however, generally much darker in colour than the rosin esters. This is chiefly because they are subjected to the destructive running process before esterification.

Pale coloured copal esters are obtainable but they are very expensive. This paleness of colour is frequently obtained by using a rosin flux or a catalyst which may be a zinc compound. In many instances the presence of either of these substances may be a serious drawback and it is often necessary to examine copal ester for their presence.

Copal esters have good solubility and compatibility, although not so good as the rosin esters. They are soluble in aliphatic and aromatic hydrocarbons, turpentine and drying oils both unpolymerised and polymerised, but insoluble in ethyl alcohol and acetone. After esterification the acid value of copal is reduced to 10–15. This is appreciably higher than the acidity of rosin ester but for many purposes is not a disadvantage.

From the varnish makers' point of view it is much more easily manipulated than the straight copal and it is not subject to the same process losses.

Copal esters possess good alkali and acid resistance, good water resistance and good durability with gloss retention. They are claimed to have little blooming tendency and exhibit little yellowing on exposure. Copal esters may retard the dry of linseed oil varnishes slightly but no retardation is noticeable with wood oil varnishes.[8]

Copal ester varnishes have good adhesion to metal when baked and have excellent flexibility.

Uses

Probably the most important use for copal ester is in the manufacture of media for hard gloss paints and enamels. Because of the low acidity of these media as compared with similar media based on

unmodified copals no precautions are necessary in the use of pigments. Basic pigments may be used, and providing that a sufficiently pale copal ester is obtainable a proportion of zinc oxide can be added, if desired, in whites or tinted whites without fear of excessive feeding. Copal esters may be used also with wood oil in good grade non-feeding gold-sizes. Another important use for these resins is in tin printing varnishes, especially the gold stoving types. They yield hard, tough, flexible films which stand stamping and are very resistant to the action of natural juices from fruit, vegetables, etc. In conjunction with wood oil, varnishes with good alkali resistance can be formulated. Gardner and Holdt found that a copal ester varnish resisted satisfactorily a 20 per cent caustic soda solution for seven days. Similar varnishes with copal broke down.[9]

They are used also for an intermediate grade of boat varnish also based on wood oil, which for quality is between the rosin or ester gum type and the modified phenolic type.

Their low acidity also makes them valuable in the production of impregnating insulating varnishes for coils or fabric.

Solutions of copal esters in solvents are sometimes added to alkyd resins to improve hardness. They are used also to some extent in the manufacture of cellulose lacquers.

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CHAPTER 7

SYNTHETIC RESINS

ALKYD RESINS

Introduction.—The many reaction products of polyhydric alcohols and polybasic acids are known either as alkyds or glyptals. The fundamental basis for these resins is the product from the direct interaction of glycerol and phthalic anhydride or phthalic acid. This product is of little value in itself, and it is only when modifying ingredients are introduced that valuable synthetic resins are produced.

Mechanism of the Resin Reaction.—Opinions have been expressed on the courses of the reactions involved by the following :—

Kienle [21] and Hovey ; Carothers ; Barry, Drummond and Morrell ; Bradley ; Savard and Diner ; Hönel ; Bozza ; Schlenkert ; [1] Wornum ; Houwink and Klaassens,[2] Siddle,[5] Flory, and Kienle and Petke.[142]

The Alcohol Component and its Effect on Resin Properties

Resins have been made from many different polyhydric alcohols but by far the most important alcohol used commercially is glycerol. The alcohol used controls to a marked degree the physical properties of the resin obtained with phthalic anhydride. Thus ethylene and propylene glycols yield non-heat convertible hard glassy resins ; diethylene glycol yields a non-heat convertible soft resin ; methyl alcohol does not yield a resin ; glycerol, pentaerythritol, and mannitol yield heat convertible hard resins.[3] With dibasic acids glycols yield fusible resins, and with polybasic acids containing more than two carboxylic groups insoluble resins are obtained.[4] Pentaerythritol, polyglycerol and sorbitol react with phthalic anhydride more readily than glycerol and yield more complex resins.[1] *Mixtures of polyhydric alcohols may be used. Partial replacement* of glycerol by glycol yields more soluble resins. 2,3-butylene glycol, trimethylene glycol and propane-1,2-diol yield more soluble resins than glycerol.[6]

Glycerol may be substituted in part by monohydric alcohols such as ethyl, amyl, butyl, allyl, diacetone alcohol, borneol, and cyclohexanol. The reaction products with phthalic anhydride are soft, water resistant and flexible.[7]

Phthalic anhydride and ethylene glycol condensed in equimolecular proportions yield a resin opaque to ultra-violet and infra-red light.[8] A resin is obtained, on heating, from phthalic anhydride, glycerol and an ethylenic or paraffinic monohydric alcohol such as lauryl alcohol. Cetyl alcohol may replace lauryl alcohol.[9] B.P. 396,354 mentions the use of tetramethylene glycol and B.P. 394,000 includes benzyl alcohol. Diethylene glycol is condensed with phthalic anhydride to form a resin.[10]

Gardner, Krauss and Van Heuckeroth have prepared a resin from

phthalic anhydride, tartaric acid and triethylene glycol.[11] The mono-ethyl ether of diethylene glycol, glycerol and phthalic anhydride are reacted together at 225° C.[12]

Ricinoleyl alcohol and phthalic anhydride are heated, at 120° C., for several hours to procure a resin which becomes infusible and insoluble on further heating.[13] Butyl alcohol, ethylene glycol and phthalic anhydride are reacted together.[14] An air-drying resin is made from abietinol, glycerol, phthalic anhydride and linseed oil, by maintaining the mixture at 250° C. for three to four hours. Abietinol is obtained from abietic acid by reduction.[15] The reaction product of 2 . 3 . dichloropropanol and castor oil soap on heating with phthalic anhydride provides an oil soluble resin.[16] Mono and diglycerides are sometimes used to replace glycerol, but this aspect is covered later under the discussion devoted to methods of manufacture.

A resin is recorded from the condensation of a mixture of glycerol and glyceryl mono, di and triacetates with phthalic anhydride.[17] Nitrocellulose resins can be made from ether alcohols (glycerol mono-ethyl ether) and phthalic anhydride. Cellulose and phthalic anhydride react in the presence of pyridine.[18]

The Acid Components and their Effect on Resin Properties

Phthalic anhydride, oleic acid, cellulose ether and glycerol are heated together at 200° C. to yield a neutral resin soluble in aromatic hydrocarbons.[19] Resin plasticisers can be made from the interaction of mono, di or triethanolamine and phthalic anhydride. Drying oil fatty acids may be introduced into the reaction mixture also.[20]

Phthalic anhydride can be replaced also by many mono, dibasic or even polybasic acids. The acids may be the fatty acids from vegetable oils or acid resins like rosin or the copals. Mixtures of mono and dibasic acids are frequently used, and phthalic anhydride may be replaced wholly or partly by these mixtures.

Acidic Resins.—Rosin, Congo, phthalic anhydride and glycerol form a resin based on natural acids. Kauri, masticated Congo copal, shellac, and tall oil fatty acids are also cited as resin components.[21]

The inclusion of rosin in air-drying alkyds improves their solubility in aliphatic hydrocarbons but reduces their durability. To introduce shellac it is heated with a polyhydric alcohol. The product is reacted with fatty oil or resin acid and then reacted with a polycarboxylic acid. Alternatively, the shellac may be heated with the fatty oil or resin acid and the resultant product reacted with a polyhydric alcohol followed by treatment with a polycarboxylic acid to effect esterification. The resins obtained are claimed to yield valuable varnishes for food containers or for electrical insulation.[22] Products obtained from tall oil fatty acids have no outstanding properties. They are miscible with nitrocellulose. A varnish of good durability is obtained by blending four parts of linseed oil stand oil with one part of tall oil modified alkyd.[21]

Vegetable Oil Fatty Acids.—Drying oil fatty acid modified alkyds are used more widely than any other modification. The following selections will demonstrate that fatty acids from almost every known vegetable oil form valuable components of all types of alkyd resins. Walnut oil fatty acids are condensed with phthalic anhydride and glycerol.[23] Other fatty acids condensed with phthalic anhydride and glycerol include stearic, a mixture of rosin and stearic acid, cottonseed, linseed, wood oil, perilla, soya bean oil, oleic, octadecadienic, coconut oil, linoleic, poppyseed, olive, castor, sesamé, colza, Japanese fish oil, and rubberseed oil fatty acids.[24]

Diethylene glycol, phthalic anhydride and oleic or palmitic acids yield a resin.[25] Oil and petrol-proof varnishes are made from a resin produced by the interaction of ethylene glycol, glycerol, phthalic anhydride, succinic acid a d fatty acids from cottonseed, linseed or tung oil.[26] Resins of much improved colour are obtained if vacuum distilled fatty acids are used. A resin is made in the presence of carbon dioxide by condensing together phthalic acid, distilled linseed oil fatty acids and glycerol.[27]

Other Monobasic Acids.—Other monobasic acids, incorporated in alkyds, include naphthenic, acetic, benzoyl benzoic, lactic and hydroxybutyric acids. An alkyd resin is based on a mixture of drying or semi-drying oil fatty acids and naphthenic acid. Polyhydric alcohols are partly esterified with naphthenic acid and then completely esterified with polybasic acid. Alternatively, naphthenic acid is used to esterify a polybasic acid containing an hydroxyl group and the product esterified by addition of polyhydric alcohol.[28]

A resin miscible with nitrocellulose is made by heating hydroxybutyric acid, vegetable oil fatty acids, phthalic anhydride and glycerol at 260°–300° C.[29]

Lactic acid or its anhydride is first reacted with a dicarboxylic acid with the object of esterifying the hydroxyl group. The resultant product is then completely esterified in a further reaction with a polyhydric alcohol.[141]

Short chain monobasic aliphatic acids with not more than five carbon atoms have been suggested for use in alkyd resins. Resins miscible with ordinary varnish resins and asphaltums are made by reacting the reaction product from acetic acid and glycerol with linseed oil fatty acids and maleic anhydride in the presence of naphtha.[30]

An interesting blue coloured resin with valuable electrical properties is claimed by reacting glycerol, phthalic anhydride and an amino-carboxylic acid together. The amino-carboxylic acid can be prepared *in situ* from $PhNH_2$ and $ClCH_2COOH$.[31]

The introduction of monobasic acids to alkyd resins is claimed to improve flexibility, a property which generally increases directly as the molecular weight of the acid.

Maleic Anhydride.—Of dibasic acids used in place of phthalic anhydride maleic acid or anhydride is one of the most important. Maleic anhydride

gives valuable products because it not only acts as a dibasic acid but acts also as an unsaturated compound. The unsaturated linkage aids further polymerisation, resulting in improved dry.

If unsaturated drying oils or their fatty acids are present these also may react with maleic anhydride to produce further complexity. If the oils contain conjugated double bonds the reaction proceeds according to the Diels and Alder synthesis. The presence of rosin helps complexity.

Maleic anhydride, by reason of its chemical constitution behaves quite differently from phthalic anhydride in alkyd resin reactions. Phthalic anhydride is capable of easy manipulation, but resins based entirely on maleic anhydride need special methods. Mixed resins containing both phthalic and maleic anhydrides enjoy some popularity, possibly because they are easier to formulate and to manufacture than the straight maleic resins.

Long oil, oil-soluble alkyds can be made by reacting phthalic acid, maleic acid, glycerol and oil fatty acids together if the maleic acid does not amount to more than 15 per cent of the phthalic acid.[32] If the proportion of oil fatty acids is substantially increased, the proportion of maleic anhydride can be increased also.[32]

Rosenblum states that the amount of maleic acid which it is possible to incorporate is limited, and that non-homogeneous products are obtained by the direct reaction of vegetable oil fatty acids, maleic anhydride and glycerol. If, however, a partial ester is first prepared from the fatty acid and glycerol, its subsequent reaction with maleic anhydride produces homogeneous resins.[33]

It has been stated that the reason for the non-homogeneity of oil modified alkyds, produced by the direct substitution of phthalic by maleic anhydride, is the side reaction between the unsaturated fatty acids and the maleic anhydride.[145]

Bevan believes this explanation to be improbable on experimental findings. Homogeneous reaction products are obtained when the initial ester formed from acid and polyhydric alcohol is insoluble in water. The presence of a mutual solvent like cyclohexanol is claimed to produce homogeneity. Other methods for obtaining homogeneous products are to react the ingredients, glycerol, maleic anhydride, and oil fatty acids in the presence of a volatile acid like acetic acid, or to first prepare a partial ester from acetic acid and glycerol.[34]

Phthalic acid or anhydride, vegetable oil acids, maleic acid or anhydride, rosin, and glycerol are condensed together at 170°–240° C. to form a resin. A resin is produced from the direct interaction of maleic acid and glycerol which is soluble in acetone, ethyl alcohol or ethyl acetate.[35] Thermo hardening resins suitable for stoving at 130° C. are produced by reacting an unsaturated aliphatic polybasic acid with a polyhydric alcohol in the presence of benzoyl peroxide, the polymerisation catalyst being added after partial condensation.[36] Maleic acid is said to react more rapidly than phthalic acid.

Maleic acid-oil modified alkyds are said to give paler resins than straight phthalic anhydride resins and to have improved colour retention, durability, adhesion and water resistance.

Maleic acid also forms heat- and oxygen-convertible resins with dihydric alcohols.[37]

Other Polybasic Carboxylic and Miscellaneous Acids.—Phthalic acid may be substituted by iso, terephthalic or hexahydrophthalic acids.[38]

Linoleic acid, isophthalic acid and glycerol have been condensed to form an air-drying composition, and the use of terephthalic acid for this purpose is also recorded.[39] Hovey[40] reports difficulty in producing alkyd resins based on terephthalic and isophthalic acids.

A comprehensive list of dibasic carboxylic acids, in addition to the above, which have been recorded as constituents of alkyds includes sebacic, adipic, succinic, oxalic, malic, tartaric, fumaric, citric, glutaric, pimelic, suberic, azelaic, malomalic, aconitic, diglycollic, thiodiglycollic, dilactic, salicylacetic, dihydracrylic, tetrahydrophthalic, camphoric, benzophenone-2,4′-dicarboxylic, diphenic, 1,8-naphthalic, dihydronaphthalene-1 : 4-dicarboxylic[41] and dihydroxydiphenylmethane dicarboxylic, and tetrachlor-*o*-phthalic acids.[143]

Reaction products of rosin or terpenes with maleic anhydride yield polybasic acids which can be condensed with glycerol. Maleic anhydride also reacts with diene or terpene compounds to yield tetrabasic carboxylic acids. These provide flexible, infusible resins when condensed with long chain glycols.[42] Maleic anhydride can be made to react also with anthracene and the product further reacted with polyhydric alcohols.[43]

Another acid which has enjoyed some popularity as an alkyd constituent is known under the name of " Petrex " which is chiefly 6-methyl-3-isopropyl-3 : 6-endoethylene-Δ^4-tetrahydro-*o*-phthalic anhydride.

A resin is obtained by the condensation of succinic acid, phthalic anhydride, rosin, glycerol, ethylene glycol and tung oil.[44] A detailed patent describes the manufacture of resins from the interaction of a polyhydric alcohol, a polybasic aromatic acid, a dibasic aliphatic acid and a dihydric alcohol. The polyhydric alcohols include glycerol, mannitol and pentaerythritol ; the polybasic aromatic acid is phthalic acid ; the dibasic aliphatic acids include succinic, malic, maleic, fumaric, glutaric, adipic, pimelic, suberic, azelaic, and sebacic acids ; and the dihydric alcohols include ethylene, diethylene, propylene and tetramethylene glycols. An alkyd recommended for patent leather is made by reacting together linseed, tung, perilla or soya bean oils or fatty acids with glycerol, pentaerythritol, or polyethylene glycol and with phthalic anhydride, succinic, fumaric, maleic or adipic acids. Other ingredients may include rosin, ethylene glycol, glycol ether or benzyl alcohol.[45] An oil-soluble resin is made from succinic acid, vegetable oil fatty acids, phthalic acid and glycerol.[46] Four molecules of monolinolein, three molecules of maleic or succinic acid and one molecule of phthalic anhydride are condensed together to yield a resin. Alternatively, resins free of phthalic anhydride are

prepared by making a di-ester from vegetable oil fatty acids and glycerol and reacting it with maleic anhydride or acid; or succinic acid is reacted with monolinolein.[47] Glycerol, phthalic acid, linoleic acid and a dicarboxylic acid such as succinic, tartaric, maleic, malic or fumaric acid, and boric acid are heated together until a resin soluble in toluol is obtained. The resin is suitable as a base for white baking enamels.[48]

The resins obtained from glycerol and adipic or sebacic acids remain rubbery even after stoving. Initially they are soft and plastic.[1] A satisfactory resin is claimed from the interaction of glycerol and succinic acid in the proportion of one part to two parts. The hardness of the resin increases directly as the proportion of acid. Callahan claims that whilst glycerol and phthalic anhydride yield brittle resins, resins from glycerol and succinic acid are tough and flexible.[49] Malic acid and glycerol yield a sticky fusible resin. Prolonged heating produces infusibility. Low temperature treatment of citric acid and glycerol provides a hygroscopic product, the hygroscopicity of which is reduced by raising the temperature of reaction. A colourless resin is produced from citric acid and glycerol.[50] Dihydroxydiphenylmethane dicarboxylic acid, wood oil fatty acids or rosin, and glycerol are reacted to yield a resin.[51]

In addition to the hydroxy acids, malic, tartaric and citric acids already mentioned, other similar acids have been protected as resin constituents. Citric, tartaric, salicylic, glyceric, glycollic and lactic acids are used to esterify glycerol, glycol or mannitol and the product condensed with phthalic, adipic or succinic acids. The resins obtained are useful for lacquers or varnishes, being soluble in alcohol-benzene or in acetone.[52]

The reaction product of lactic acid, phthalic anhydride and ethylene glycol is a resin.[53]

Boric Acid.—Boric acid sometimes occurs as a constituent of alkyd resins. The products of interaction of polyhydric alcohols with boric acid are generally water soluble. A resin may be prepared from glycerol and phthalic anhydride in the presence of boric acid. These products may be used as adhesives or as plasticisers for glues. Glycerol, 200 parts; phthalic anhydride, 148 parts; and boric acid, 62 parts, are reacted at 200° C. for three hours, when linoleic acid, 280 parts, is added. Heating is continued at 240° C. until the product is soluble in toluene. The resin is blended with nitrocellulose to confer gloss and durability. A fatty acid with more than thirteen carbon atoms, glycerol, phthalic acid and boric acid are condensed together to form a resin.[54]

The presence of boric acid in a resin is said to increase the complexity. Thus, phthalic anhydride, polybasic aliphatic acid, vegetable oil fatty acids, boric acid, natural resin and glycerol are heated together.[55]

Vegetable Oil Modified Resins

Linseed Oil.—Esters are common constituents of alkyds, especially in the form of triglycerides such as vegetable oils. Thus phthalic anhydride and linseed oil are heated together, glycerol added and the

mixture heated further to form a resin, or the product obtained by condensing phthalic anhydride and glycerol is heated with linseed oil at 200°–220° C., more glycerol added and the heating continued at 240°–260° C.[56] The reaction product of phthalic anhydride, three molecules, and glycerol, four molecules, is heated with a non-hydroxylated vegetable oil ; more phthalic anhydride is added and the heating process continued.[57] A preheated drying oil, phthalic anhydride and a drying oil acid monoglyceride form an oil soluble resin.[58]

Sulphurised Oil.—Sulphurised linseed or wood oil is reacted with glycerol and phthalic anhydride to yield a soluble resin. Alternatively, the oil may be sulphurised in presence of the other ingredients.[59]

Ongokea Klaineana Oil.—A resin suitable for use in varnishes is produced from phthalic anhydride, glycerol and oil of Ongokea Klaineana.[60]

Castor Oil.—Castor oil is a very popular oil for alkyds whether of the air-drying or stoving types. Thus castor oil, phthalic anhydride and glycerol yield a benzene soluble resin on heating. If the reaction is conducted at 260°–270° C. the resin has drying properties, or the phthalic anhydride and glycerol are given a preliminary heating at a relatively low temperature (150° C.) when the castor oil is added and the process continued at 260°–270° C. Solubility in aliphatic hydrocarbon is attained by increasing the oil content of the resin. Castor oil, ethylene glycol, and phthalic anhydride are condensed together. Octadecadienic acid, castor oil, glycerol and phthalic anhydride provide a useful resin.[61] A product soluble in organic solvents is derived from phthalic acid and hydrogenated castor oil.[62]

Tung Oil.—Wood oil is a difficult oil to incorporate in alkyd resins. A product is obtained by heating glycerol, rosin and wood oil until homogeneous, phthalic anhydride is then added, and the mixture condensed further.[63]

Special Modifications

Waxes.—Waxes have been used as modifying agents for alkyds. An ester type wax such as montan, beeswax, carnauba, or spermacet wax is heated with glycerol in the presence of a catalyst and the product reacted with phthalic anhydride.[64]

Halogenated Alkyds.—Halogenated alkyds have been recorded. The product from castor oil, polybasic acids and polyhydric alcohols is dissolved in benzene or carbon tetrachloride and chlorine or bromine is added until 5–25 per cent is absorbed, based on weight of resin.[65] Halogenated castor oil alkyds are used as flameproof plasticisers. Glycerol, phthalic anhydride, monobasic acid and drying oil are treated with 1–2 per cent. halogen based on the oil and then reacted together. Alternatively, the oil may be treated with halogen.[66]

Urea.—Modification of alkyds by urea compounds either by direct interaction or by simple addition yields valuable stoving media. Urea, glycerol and phthalic anhydride are reacted together, or the urea and

phthalic anhydride may be heated, after which the glycerol may be added and the reaction continued.[67] A urea-formaldehyde resin and an unmodified alkyd are mixed in butyl alcohol and reacted.[68] Such resins are used as colourless, hard, rapid stoving lacquers.

An alkyd comprising castor oil, phthalic anhydride and glycerol is dissolved in butyl alcohol. Urea and paraformaldehyde are added and the mixture refluxed. The resultant resin may be used with nitrocellulose.[69] Unmodified alkyds with urea-formaldehyde yield hard products, whilst castor oil modified alkyds yield pale flexible resins.[70]

Vinyl Compounds.—Vinyl modified alkyds are recorded.[71] The condensation of polyhydric alcohols and polycarboxylic acids with monobasic acids having more than six carbon atoms is conducted in the presence of polyvinyl acetate, propionate or butyrate.

Phenol Formaldehyde Resins.—Another very useful modification of alkyd resin, which is gradually assuming some popularity, is the incorporation of phenol formaldehyde resins. Glycerol phthalate monoester is prepared from glycerol and phthalic anhydride ; rosin and linseed oil fatty acids are then added, followed by a cresol-formaldehyde product. Linseed oil is added finally and the mixture heated at 280° C.[72]

A similar resin suitable for use in lacquers is made as follows : glycerol and phthalic anhydride are first condensed at 160°–170° C., rosin and linseed oil fatty acids are then added. Finally, a reaction product of *m* and *p*-cresol with formaldehyde is incorporated.[73]

A cresol-formaldehyde product is added to molten rosin. Phthalic acid and glycerol are added and the reaction completed at 270° C. A tough resin soluble in aromatic hydrocarbons is obtained.[74] Megson and Holmes [75] heat all the ingredients, glycerol, polybasic acid, phenol and paraformaldehyde together to form a resin. Rosin, phenol, and phthalic anhydride are heated together at 110° C., formaldehyde is then added followed by further heating. Glycerol is added to esterify the acidity and a resin soluble in vegetable oils and suitable for use with nitrocellulose results.[76]

Glycerol and a drying oil are added to a preheated blend of wood oil and phenol-formaldehyde resin, and the whole heated until homogeneous. Phthalic anhydride is added and the heating continued.[77]

An alcoholic solution of sulphuric acid is added to phenol formaldehyde-alkyd lacquer to accelerate the hardening. The curing of alkyd resins is greatly facilitated by the addition of small amounts of phenol-formaldehyde resin.[78]

The Manufacture of Alkyds

Methods used for the manufacture of alkyds vary considerably. The plant most commonly used comprises a large pot which is either aluminium or stainless steel. The pot will be fitted with a mechanical stirrer, capable of agitating the reaction mixture gently from the bottom upwards. Gentle agitation results in more rapid heat transference,

with economy in fuel, less local overheating causing decomposition with loss of colour or excessive polymerisation, and less risk of fire. Methods of heating include coke, oil, gas or electrical immersion heaters. The pots may be totally enclosed except for charging hatches or to permit introduction of stirring gear, etc. The plant is constructed to permit the introduction of a carbon dioxide supply tube as well as to include a "draw-off." The "draw-off" may pass into air-cooled condensers for trapping volatilised phthalic anhydride. This is collected and used again. An improved method for collecting volatilised phthalic anhydride has been described,[79] in which the deposition of phthalic anhydride in the outlet pipe from the pot is prevented by keeping this pipe hot. After passing through the hot pipe the vapours pass into a collecting vessel and from thence to a contact spray condenser. The phthalic anhydride is pumped away as a sludge. Glycerol which is volatile in steam may also tend to distil over, especially if the reaction is conducted at high temperatures. Plant design may minimise this, although an excess of glycerol can be introduced initially and any glycerol distillate can be used again. It is frequently necessary to discontinue the reaction abruptly to avoid over-polymerisation of the reactants and this may be accomplished either by running or pouring off the hot resin into a tank containing cold solvent, fitted with a stirrer, or to immerse the reaction pot and contents in a large bath of cold water.

Siddle [97] has, however, emphasised that the production of alkyds of uniformly good quality is a difficult procedure from simple equipment. An improved method of heating, which is of recent development, is by the circulation of hot vapour. The Dowtherm system is typical, and is claimed to be especially satisfactory for the manufacture of alkyd resins.[106] The range of temperature which may be covered by this method is from 200°–400° C. Among the many advantages of heating by the condensation of Dowtherm vapour, is the avoidance of local overheating. The whole of the heating surface is subjected to a single definite temperature. General overheating is prevented by controlling the temperature of the Dowtherm. Absence of local overheating results in more homogeneous polymerisation, and a more certain end-point, besides producing a substantial reduction in loss of phthalic anhydride.

The Dowtherm is vapourised in a gas or oil fired boiler, and the vapour condensed in the jacket or coils of the reaction vessel. Pressures developed in the system are low, for at 320° C. the boiler pressure is only 35 lb. per square inch. Dowtherm has an atmospheric boiling-point of 258° C. For reaction temperatures below 240° C. the boiler is run generally at slightly above atmospheric pressure, and control is exercised by regulating a valve. Where substantially lower temperatures are required, the whole heating system can be run at reduced pressure.

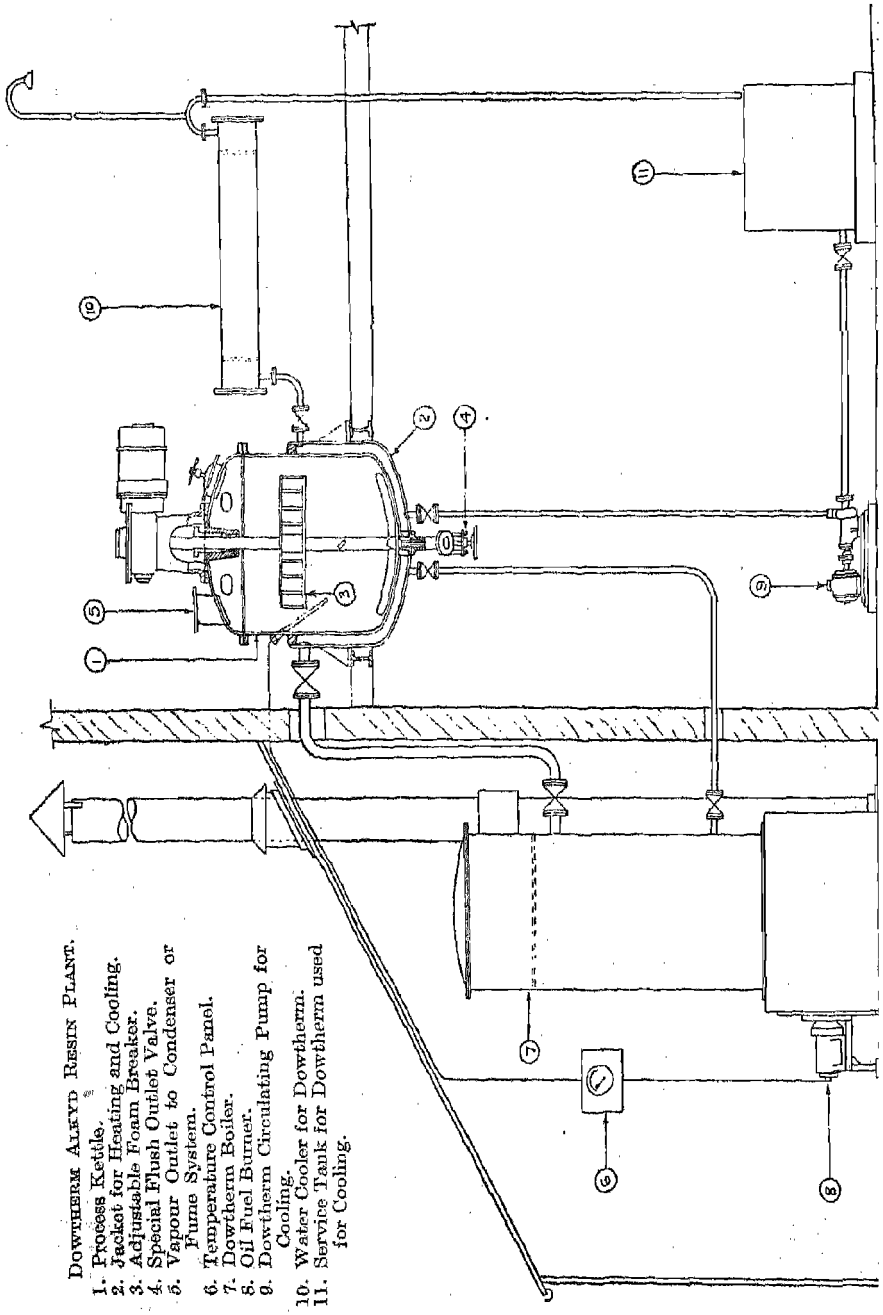
Good temperature control of the Dowtherm is obtainable in this system, by means of a thermostat at the boiler, and it is easy to control temperatures to within $\pm$ 2° C. Where large plants are in operation the

maximum temperature variation of the reaction vessel will have evened out to $\pm 0{\cdot}5°$ C. The system as shown in the diagram includes a water cooler. It is thus possible to cool the reaction vessel rapidly as required. Rapid cooling is obtained by circulating cooled liquid Dowtherm in the jacket. The vapour and condensate valves are closed, liquid inlet and outlet valves opened, water is turned on the cooler, and the circulating pump started.

The methods of conducting the reaction for the formation of alkyds vary considerably. For unmodified alkyds containing only glycerol and phthalic anhydride the two reactants may be mixed and reacted by heating. When the reaction has reached a convenient stage it is discontinued and the resin dissolved in solvents. After glycerol and phthalic anhydride have been reacted by heating, a reduced pressure (2 inches Hg) is used to remove uncombined reactants. It is claimed that the extent of the reaction may be estimated by measuring the amount of water generated.[80]

Glycerol and phthalic anhydride are heated until gelation begins, when a high boiling dialkyl ester of an organic acid is added and the heating continued further.[81] An alkyd with controlled polymerisation is obtained by reacting glycerol and phthalic anhydride until a powderable resin is obtained. The powdered resin is then polymerised further, by heating in a rotating drum at 100° C. with the temperature rising to 200° C. or above.[82] Resins of low acidity are made by dissolving the reaction product of glycerol and phthalic anhydride in a suitable organic solvent and neutralising with mild alkali. This causes the precipitation of a resin with an acid value of zero and the formation of the sodium salt of phthalic acid. The resin, soluble in alcohol or acetone, is obtained by evaporating the solvent under reduced pressure.[83] When the reaction between glycerol and adipic acid is partly complete the product may be neutralised with ammonia and heated further.[84]

For oil modified alkyds where the ingredients are fatty acid, glycerol and phthalic anhydride all three ingredients may be heated together. Resins containing organic acids other than phthalic acid are made by the same method, for example, glycerol, phthalic and maleic acids with fatty acids are reacted together.[85] Rosin, phthalic anhydride, masticated Congo copal and glycerol, on heating for thirty minutes at 230° C. are claimed to yield an oil-soluble resin.[86] A natural resinous hydroxy acid contained in a soluble masticated Congo copal, is reacted with a polyhydric alcohol, a non-hydroxy monobasic carboxylic acid and a polybasic carboxylic acid to yield a good durable resin.[87] Coconut oil fatty acids, stearic acid, phthalic anhydride and glycerol are reacted in an atmosphere of carbon dioxide or nitrogen at a maximum temperature of 250° C. A resin soluble in toluene or butyl acetate, with softening point of 64° C. and acid value of 22 is obtained.[88] Fatty acids from linseed, soya bean, tung, perilla, poppyseed, castor, olive, sesamé, colza or Japan fish oil are heated at 230° C. for twenty hours with phthalic



Dowtherm Alkyd Resin Plant.

1. Process Kettle.
2. Jacket for Heating and Cooling.
3. Adjustable Foam Breaker.
4. Special Flush Outlet Valve.
5. Vapour Outlet to Condenser or Fume System.
6. Temperature Control Panel.
7. Dowtherm Boiler.
8. Oil Fuel Burner.
9. Dowtherm Circulating Pump for Cooling.
10. Water Cooler for Dowtherm.
11. Service Tank for Dowtherm used for Cooling.

anhydride, glycerol and maleic, malic, succinic, or fumaric acids. The resultant resin is miscible with drying oil and aromatic hydrocarbons. It is claimed, moreover, that if the percentage of fatty acids is kept low the resin is miscible with nitrocellulose also.[89] Soluble lacquer resins are made by reacting a monocarboxylic acid, a polycarboxylic acid and a polyhydric alcohol in xylene at 230°–250° C. under pressure.[90] Esterification of distilled polymerised fatty acids and phthalic anhydride with glycerol is recorded.[91]

Another method of manufacture is to heat first some of the ingredients and when this reaction has progressed to a convenient stage to add the remainder and continue the process. Oleic acid, phthalic anhydride and glycerol are condensed at 280° C., more glycerol and phthalic anhydride added and the reaction continued at 230° C. The resin obtained is soluble in aromatic hydrocarbons, turpentine and vegetable oils. A similar product is obtained by heating olein, phthalic anhydride and glycerol at 200° C. for several hours. More glycerol and phthalic anhydride are added and the heating continued at 190° C.[92]

An oil soluble resin is made by heating part of the phthalic anhydride with glycerol and linseed oil fatty acids for several hours. The rest of the phthalic anhydride is added and the reaction continued.[93]

An infusible glyceryl phthalate product is first formed and this is reacted with a glycerol ester containing free hydroxyl groups. The glycerol ester is derived from vegetable oil fatty acids, phthalic and abietic acids.[94]

When a vegetable oil is a resin component its incorporation may cause substantial adjustments in procedure, although it may be reacted as such with the other components, without preliminary treatment. At room temperature, glycerol, linseed oil fatty acids, drying oil and phthalic anhydride are allowed to combine to form a homogeneous mixture. On heating a resin is produced.[95]

The drying oil and phthalic anhydride may be heated until the blend is homogeneous when the glycerol is added and the process continued.[96] In a similar process phthalic anhydride and linseed oil are heated under reflux at 270°–300° C. after which glycerol is added.[97] A resin is made from phthalic anhydride, glycerol, diethylene glycol and coconut oil.[98]

The condensation of polyhydric alcohols and polycarboxylic acids is conducted in the presence of stearic or oleic acids. The product is heated with small quantities of drying oils. Larger amounts of drying oil are added and the whole maintained at 270° C., until ester interchange is complete. Hard, air-drying, tack-free varnishes are claimed.[99]

It is difficult to produce resins containing tung oil which are free from webbing tendency. An oil-soluble resin from tung oil is recorded.[100] Polybasic aliphatic acids like maleic, fumaric, malic and succinic acids are reacted with phthalic acid, vegetable oil fatty acids and glycerol in the presence of tung oil.

Resins of good dielectric strength, suitable for insulating varnishes, are made by heating abietic acid, glycerol, phthalic anhydride, linseed oil fatty acids, and ethylene glycol, under reflux for thirty minutes at 175° C. Wood oil is added in four lots. Finally, succinic acid is added and the heating continued. Subjection of the resultant product to a vacuum distillation removes excess glycerol.[101]

The most popular method of introducing vegetable oils, such as linseed oil into alkyd resins, is by first preparing their monoglycerides and condensing these with the other normal resin components. The introduction of vegetable oils in the form of their monoglycerides is also probably the most satisfactory method of incorporation.

Monoglycerides are generally prepared by heating the vegetable oil with glycerol at elevated temperatures (270°–290° C.) with or without the aid of a catalyst.

On heating wood oil or rubberseed oil with glycerol in the presence of caustic soda the respective monoglycerides are formed. These are reacted further with more glycerol and polybasic acid.[102] Glycerol and castor oil are heated together in the presence of caustic soda and the product heated further with phthalic anhydride.[103]

Monoglycerides from soya bean oil are produced under the catalytic effect of calcium glyceroxide.[104]

A resin miscible with stand oil is made by heating a drying oil and glycerol to form a glyceride, adding phthalic anhydride and continuing the heating.[105] Wood oil monoglyceride is reacted with phthalic acid to form a resin. An improvement is claimed if the monoglyceride is blended with ester gum before condensing with phthalic acid.[106] Monoglycerides may be prepared from drying oil fatty acids and glycerol. They are condensed with polybasic acids and drying oils to form a resin.[107] A partial reaction is conducted between phthalic anhydride and glycerol, a drying oil monoglyceride is added and the condensation completed. The partial ester of glycerol and phthalic anhydride is etherified with the product of alcoholysis of rape or linseed oil with glycerol.[108]

Monoglyceride is produced by heating an oxydised drying or semi-drying oil with a polyhydric alcohol in the presence of a catalyst. Polybasic acid is added and the reaction continued. The resultant resin is heated in solution with a product of urea and formaldehyde.[109]

An ingenious Russian method for the production of alkyds is based on the use of phthalic anhydride in vapour form. The mixed mono- and the diglycerides of linseed oil are first prepared by heating linseed oil (45 pts.) and glycerol (21 pts.) in the presence of litharge (0·5 pts.), at 240° C. for forty-five minutes with constant stirring. Vapours of phthalic anhydride are passed through the hot mixture for two hours. Evidence is lacking, but if the reaction is complete after this treatment, it offers substantial advantages over the usual method using solid anhydride, with respect to saving of processing time.[144]

Alkyds produced from monoglycerides usually air dry more rapidly than resins of similar composition derived from fatty acids.

Castor oil is a common constituent of alkyd resins. The fact that it contains hydroxyl groups capable of esterification with acids makes it a very useful constituent. Products from the interaction of castor oil and phthalic anhydride make plasticising resins especially suitable for use with nitrocellulose. An acid ester is made from phthalic anhydride and glycerol. After the addition of castor oil the heating is continued.[110] Castor oil, glycerol and phthalic anhydride are heated together at 280° C. In the meantime a product of glycerol and phthalic anhydride is prepared and this, with calcium resinate, is added to the castor oil-glycerol-phthalic anhydride product and the whole heated at 180°–200° C. to form a resin.[111]

Catalysts for Alkyd Formation.—Many catalysts have been suggested for use in the manufacture of alkyd resins, some with the object of facilitating the reaction but others to have additional influences, such as preserving colour, etc. It is claimed that the reaction between phthalic anhydride and ethylene glycol is assisted by presence of sulphuric acid, bismuth subcarbonate, basic cuprous carbonate, cobalt, lithium, manganese, barium and cadmium carbonates and calcium, beryllium, copper and lithium nitrates.[112]

Zinc chloride and phosphoric acid are other catalysts suggested to aid resin formation. A water-resistant resin is obtained by reacting glycerol, phthalic anhydride, drying oils and their acids together in the presence of litharge.

The use of litharge as a catalyst is elaborated elsewhere where phthalic anhydride, glycerol and/or ethylene glycol, and linseed, soya bean, perilla, wood oil or menhaden oil or their acids are condensed in its presence.[113]

Ethylene glycol (one molecule) and phthalic anhydride (one molecule) are heated together at 110°–150° C. in the presence of 0·00025–0·00035 per cent of copper carbonate.

The presence of 0·002 per cent copper as a copper compound, based on reactants, during the condensation of glycerol and phthalic anhydride is claimed to yield alkyds with low acid values.

The presence of copper salts is said to promote decarboxylation with consequent loss of carbon dioxide and generation of benzoic acid. Under these conditions resins rich in tung oil can be produced without risk of gelation and with low acid values.[114]

A resin suitable for use with nitrocellulose is derived from the reaction between oleic acid, phthalic anhydride, and glycerol in the presence of ammonium bisulphate.[115] Metallic oxides, metals or mineral salts are suggested as catalysts for the reaction between polybasic acids and polyhydric alcohols.[116]

The condensation of polybasic acids (phthalic anhydride) and polyhydric alcohols (glycerol) is facilitated by heating the reactants at 250° C. in the presence of boric acid, boric acid esters, or B_2O_3.[117]

Concentration of Ingredients and Speed of Reaction.—Excess glycerol or phthalic anhydride reduces the speed of polymerisation of an alkyd resin, and the effect of excess glycerol is more pronounced than the effect

of excess phthalic anhydride.[118] Excess phthalic anhydride also tends to precipitate out on storage causing seediness and sometimes has an inhibiting effect on dry.

Maintenance of Colour.—The formation of coloured bodies in resins produced by condensation and polymerisation, and destructive effect of light upon them is prevented by adding a number of inorganic bodies to the reactants. Amounts of the additions vary from 0·0005 per cent to 0·05 per cent. The inorganic compounds include carbonates of cobalt, lithium, manganese, cadmium and barium, a basic copper carbonate [$Cu_2(OH)_2CO_3$], bismuth subcarbonate, nitrates of calcium and lithium, acetates of sodium, copper and manganese, hydroxides of cobalt, beryllium, copper, thorium, or finely divided metals including cobalt, silver and cadmium.[119] Formation of coloured bodies in oil modified alkyds is prevented by the addition of oil soluble organic esters of phosphorous acid to the reaction mixture.[120] If citric, tartaric or oxalic acid to the extent of 0·1 to 0·5 per cent by weight of the total ingredients is added to an alkyd resin at 200° C., in the latter stages of its formation, a bleached product is claimed. Care should be taken in making such additions since considerable frothing may occur.[121]

Production of Resins of Low Acidity.—Resins of low acidity are produced by modifications in method. Alkyds derived from polybasic and monobasic acids with polyhydric alcohols are dissolved by warming in methyl or ethyl alcohol. On cooling or by the addition of a precipitant, a resin of low acidity free from unreacted components or low molecular weight products is deposited.[122] A resin derived from phthalic and citric acids, with glycerol, is dissolved in a mixture of benzene and alcohol. The addition of more ethyl alcohol causes the separation of two layers. Low molecular weight products together with unreacted components are removed in one layer and a resin of low acidity generated from the other.[123]

Works Control of Alkyd Manufacture.—Works control of the manufacture of alkyd resins is based on the determination of certain constants and their comparison with similar constants of a standard laboratory made resin. A popular method of control is to dissolve the works' resin in a given quantity of solvent and to compare the resultant viscosity with that of a standard resin thinned similarly. When both viscosities are identical, the reaction is discontinued. Check tests may be made by the determination of acidity, but this procedure may be deceptive. Apart from any free acid present, acidity may be due to carboxyl groups actually present in resin molecules. Bhattacharya has suggested that the course of the reaction is best followed by the determination of hydroxyl values.[1]

Comparison of Alkyds and Natural Resins

Kolke [124] claims superiority of alkyds over natural resins for the following reasons: Firstly, the constancy of quality which is obtainable;

secondly, the low losses incurred in manufacture and finally the simplicity in use, for alkyds do not require any complicated heat treatment for oil blending if the correct type of alkyd is chosen.

Classification of Alkyds

From the varnish maker's point of view, alkyds may be divided into the following groups: unmodified glyceryl phthalate resins, drying oil modified resins, non-drying oil modified resins, natural resin modified resins and synthetic resin modified resins. Kolke [124] has suggested another classification; alkyds for air-drying varnishes, compatible with stand oil, natural and synthetic resins, alcohol and zinc oxide; alkyds for baking varnishes yielding hard glossy films with similar compatibility to the air-drying alkyds; and alkyds for use with nitrocellulose.

Unmodified Alkyds

Properties.—Unmodified alkyds are the least popular of the range probably by reason of their relatively poor solubility, necessitating the use of expensive solvents. A resin solution derived from glycerol and phthalic anhydride may be baked on to chromium plated steel to form a film which is capable of removal and application to any other surface without baking.[125] Another use for unmodified alkyds is as adhesives.

Drying Oil Modified Alkyds

Properties.—Drying oil modified alkyds are those resins capable of drying by oxidation, particularly in the presence of the common drying metals.

Solubility.—The longer oil type are soluble in aliphatic hydrocarbons, but as the fatty acid content diminishes stronger solvents are necessary to effect solution; turpentine-white spirit mixtures, turpentine, and mixtures of these solvents with aromatic hydrocarbons (xylol and naphtha), or aromatic hydrocarbons may be used, in this order, as the fatty acid content diminishes. Fawcett claims that solubility increases with degree of saturation of fatty acid constituent.[126] Among the outstanding properties of air-drying alkyd resins may be included the following.

Yellowing.—They have less tendency to yellowing than natural resin varnishes. If the oil or oil constituent present is at least partly soya bean or dehydrated castor oil, varnishes can be formulated with excellent colour retention. Further, the introduction of walnut oil fatty acids is claimed to yield light stable resins, as is also the incorporation of organic peroxides.[127]

Durability.—The durability of air-drying alkyds is outstanding. It is vastly superior to that of the ordinary oleo-resinous varnish and generally superior to that of pure phenolics with wood oil. Variation of durability with oil length is not so marked with alkyd varnishes as

with other types. Siddle [1] states that over the range of 30 to 65 per cent of drying oil no substantial difference in durability is apparent, and this is confirmed by the author's own experience. Gloss retention is better with alkyds than with oleo-resinous varnishes. The gloss of alkyds is maintained if an oxidation inhibitor such as guaiacol is present.[128]

The flexibility of alkyds is greater than that of oleo-resinous varnishes of similar oil length. On the assumption that oil length, within certain limits, is the criterion of durability, an explanation is obtained which accommodates the superior durability of alkyds. Another important factor is that alkyds retain their flexibility on ageing. Siddle [1] makes an interesting claim that a linseed oil alkyd (35 per cent oil) has better durability than an oleo-resinous varnish (75 per cent oil), and a dry equal to that of a very short oil varnish (15 per cent oil). He also accounts for the outstanding durability of alkyds by pointing out that they are highly polymerised complex bodies with a close-knit structure and consequently they are not so susceptible to degradation by atmospheric oxidation as ordinary polymerised or unpolymerised oils. German workers have stressed the point of oil economy in alkyds whilst still retaining excellent flexibility.

Drying.—The drying of alkyd resins is interesting. They attain the surface dry condition rapidly but take considerably longer time to harden right through. This explains one of their defects in that they are very prone to rivelling if applied in abnormally thick coats. Further, the fact that films do not harden through rapidly means that successive coats of the same varnish applied over each other tend to soften the first coatings and stimulate rivelling. The rivelling tendency is exploited in rivelling enamels. The tendency to rivel may be minimised by the introduction of lead drier in addition to the cobalt, but this produces another defect in that turbidity of the varnish rapidly occurs. Although addition of fractional percentages of benzoic acid is claimed to obviate precipitation of insoluble lead compounds its effect is only temporary. Slight turbidity of varnish due to lead drier appears to be tolerated by most varnish manufacturers. Filtration of the turbid varnish results in only temporary success for the turbidity develops again on ageing. Experiments have shown that the turbidity is not harmful in detracting from gloss or durability of the dried film. Cerium driers can be used in place of lead to minimise rivelling tendency, and whilst no insoluble cerium compounds are precipitated from the varnish on ageing, darker varnishes which yellow on exposure are obtained. The use of cerium is not popular.

Attempts to accelerate the rate of drying of alkyds by the introduction of wood oil have not been very successful, for wood oil in alkyds seems to be unable to exert its customary drying power. Neither does the introduction of dehydrated castor oil into the resin molecule produce any substantial improvement in dry. It has been stated that drying oils which polymerise slowly on heating show the greatest improvement in dry and hardness of film when incorporated into alkyds.[1]

When alkyds dry slowly they exhibit, sometimes, a distinct tendency to web or "crow's-foot," although only linseed oil constituents may be present. When wood oil or dehydrated castor oil or their constituent fatty acids are introduced into an alkyd resin it is difficult to obtain a varnish free from webbing tendencies. This characteristic makes alkyds a popular basis for crystallising enamels.

Water Resistance.—An outstanding defect of alkyds is their low water resistance. Normal dried films absorb several per cent of moisture on immersion. The introduction of wood oil or dehydrated castor oil fatty acids effects appreciable improvement in water resistance. Scott [129] claims that after stoving, alkyds show better water resistance than oleo-resinous varnishes. The water resistance of alkyds is improved if free hydroxyl groups are reacted with a ketene.[130]

The introduction of large amounts of lead oxide into alkyd resins is claimed to improve water resistance also.[131]

Brushing Properties.—Alkyd resin varnishes do not brush so easily or flow out so well as other types of varnishes, especially on large surfaces. These defects are noticeable as a very strong pull on the brush and the tendency to retain brushmarks.

The introduction of flow-inducing agents like decalin, dipentene or pine oil is a common procedure. Reduction of viscosity of the varnish does much to minimise these troubles, but since alkyds require abnormal amounts of thinners to obtain normal varnish consistency, further reduction of viscosity by additional amounts of thinners results in poor films, with inferior gloss and protective power.

Stoutening on Ageing.—Alkyd resin varnishes show a definite tendency to stouten on ageing. Since these varnishes are normally prone to rivel, the increase in viscosity increases the possibility. The trend, therefore, to minimise this defect, is to employ the strongest solvents consistent with retention of other properties and to keep viscosities as low as possible initially.

Uses

Uses.—Alkyds are exploited in stoving lacquers and enamels, especially where discoloration is to be considered. This includes their incorporation in silver stoving varnishes and pale finishes for natural and artificial silk. In pale stoving enamels alkyds are very popular. After stoving, alkyds yield films with high dielectric strength and for this reason they form the foundation of many impregnating insulating varnishes for the manufacture of tape. An essential feature of alkyd varnishes for application to silk or cotton fabric is the ability to recover to the original film state without exhibiting permanent crease-marks, after crushing of the treated fabric. Permanent crease marks indicate rupture of the film and lack of adhesion of the film to the fabric. These are potential sources of electrical breakdown. Alkyd resins, by reason of their excellent flexibility and adhesion to the fabric, show high dielectric strengths after crushing.

Varnish Constituents

An air-dried alkyd film is very resistant to solvents, including alcohol, petrol and lubricating oil. Furthermore, if carefully formulated, they may form the basis of air-drying finishes resistant to liquid war gases such as mustard gas. Stoved films are more resistant to solvent action than those merely air-dried.

Alkyds provide excellent media for the modern synthetic enamels with rapid dry and outstanding durability. Their complex structure aids in maintaining the pigments in suspension with minimum settling. Alkyds are claimed by Wulf to be free from chalking tendency.[132] This statement is not generally true for titanium dioxide, a notorious pigment for inducing chalking, does so also with alkyds. A mixture of antimony and titanium oxides is suggested to obviate this defect.[1]

Alkyd enamels incorporating lithopone may liver. This can be eliminated if the material soluble in acetic acid is reduced to less than 0·05 per cent.[133]

Both chrome orange and zinc oxide may liver with all but alkyds of low acidity. Highly polymerised alkyds may gelate with Prussian blue but the addition of salicylic acid is claimed to overcome gelation.[1] All carbonate pigments react with alkyds with evolution of carbon dioxide on storage.[134]

Alkyds form the basis of very satisfactory anti-corrosive primers for use on metals such as steel, iron, or zinc. They are eminently suitable where adhesion problems have to be solved. The best pigments to use are zinc and basic lead chromates or red lead.[135]

The shorter variety of alkyds are used in stoving lacquers and enamels or as resin plasticisers for cellulose lacquers.

Non-Drying Oil Modified Alkyds

Properties and Uses.—Alkyd resins modified with non-drying oils are used primarily as plasticisers in stoving finishes, particularly with urea formaldehyde resins or as plasticisers for cellulose lacquers. Whilst they show only slight inclination to harden on heating the addition of a few per cent of urea or melamine formaldehyde resin yields hard, tough films if the temperature of stoving is in excess of 220° F. These films have outstanding hardness, depending upon the percentage of urea resin present, are very resistant to solvents, and retain a very pale colour even when the temperature of stoving is high (300°–350° F.). Water resistance of these films is not very high due to the presence of the urea formaldehyde resin.

These alkyds (based on non-drying oils) are useful as the basis of non-drying adhesives.

Natural Resin Modified Alkyds

Properties and Uses.—Many attempts have been made to modify alkyd resins by the addition of natural resins both during the actual formation of the resin which has been indicated already or by simple

addition to the alkyd subsequently. These modified resins are chiefly of the rapid air-drying or stoving types. Normally, incorporation of natural resin is to improve gloss, hardness and speed of dry. Whilst the introduction of rosin is stated to improve the solubility of alkyds in aliphatic hydrocarbons, the addition of other resins necessitates the use of stronger solvents if these resins are present during the initial reaction. Stock [136] asserts that alkyds generally need the addition of natural resins to obtain the best results. Addition of copal ester yields varnishes of good flexibility if the extent of the addition is limited. Good gloss is obtained but dry and hardness are not substantially improved.

A resin made from phthalic anhydride, glycerol, linseed oil and linseed oil fatty acids is blended with rosin, Congo copal or phenol formaldehyde resins by heating to effect solution.[137]

Most references to additions of damar comment favourably on its effect. Stock [136] claims that excellent varnishes are obtained. Marshall and Skett [138] have conducted experiments with alkyds and damar mixings.

Synthetic Resin Modified Alkyds

Properties and Uses.—The last group of alkyds to be considered are the synthetic resin modified alkyds. The influence of urea formaldehyde resins has been indicated already. Phenol formaldehyde resins may be incorporated in alkyds by promoting their formation from their ingredients *in situ* simultaneously with the alkyd reaction; by adding phenol formaldehyde resin to a completed alkyd resin or by blending an alkyd varnish with a phenol formaldehyde varnish. Considerable difficulty may be experienced in introducing the so-called oil-reactive pure phenolics into alkyds by heating. Much frothing occurs and polymerisation proceeds rapidly. Only small percentages of phenolic can be incorporated by this method, i.e. 5 to 10 per cent calculated on the alkyd, if risk of gelation is to be avoided. The addition of phenolic resin does improve the " through dry " of the alkyd although the surface drying time is appreciably retarded. The addition of phenolic resin also improves the chemical resistance but durability shows no substantial improvement. The great increase in the degree of polymerisation consequent upon the incorporation of phenolic resins results in the necessary addition of excessive amounts of thinners to obtain normal varnish viscosity. This in turn results in poorness of film. From the aspect of air-drying varnishes or enamel media the best method of blending alkyds and phenolics is described in the section on phenol formaldehyde resins.

The addition of maleic resins to alkyds, more particularly for stoving finishes, by dissolving by heating or by blending with a solution of maleic resin in a solvent, is adopted primarily to yield harder films. Maleic resins are themselves quite hard and with alkyds they yield films with little tendency to discoloration on stoving.

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PHENOL FORMALDEHYDE RESINS

Unmodified Resins

General Reaction between Aldehydes and Phenols.—Baeyer showed that the reaction between phenols and aldehydes is a general one,[1] and much work since completed is of academic interest only. Resins have been made from phenols such as pyrogallol, resorcinol, orcinol, phenol and α-naphthol by reaction with benzaldehyde. Similar reactions have been conducted with formaldehyde.[2] Acetaldehyde has been reacted with phenol and resorcinol, and salicylaldehyde with phenol. Other aldehydes used include butyraldehyde, vanillin, oils of cassia and cinnamon, and acrolein. Of all the reactions studied there are only a relatively small number which have found favour commercially. These are recorded later.

Condensing Agents.—Many different condensing agents which facilitate the reaction have been patented. They may be divided roughly into two main classes based on alkalinity and acidity. In the former class are included compounds of ammonia (carbonate, hydroxide); compounds of sodium (hydroxide, cyanide, acetate, sulphide, borate, phosphate, alcoholate, formate, aluminate, tungstate, zincate, salicylate); compounds of potassium (hydroxide, carbonate, acetate, cyanide, sulphide); hydroxides of calcium, barium, strontium, copper, and aluminium; lead oxide. Organic compounds including urea, guanidine carbonate, dithiocarbamates, aniline, dimethylaniline, pyridine, amino phenols, methyl amino phenols, hydroxyquinoline, acetanilide, furfuramide, and hydrobenzamide, have been used, as well as hexamethylenetetramine and its salts, and hydroxylamine and hydroxydiphenylamine. Holmes and Megson [3] have studied the effectiveness as condensing agents of a further range of amines, and yet a further list are included in B.P. 302,609.

Among the acidic condensing agents are acids such as hydrochloric, sulphuric, tartaric, oxalic, acetic, phosphoric, boric, formic, citric, lactic, gallic, tannic; organic acid chlorides (acetyl chloride, benzoyl chloride); benzyl chloride; sulphuryl and sulphur chloride; phosphorus penta and oxychloride; esters of sulphuric acid; hydrogen sulphide; sulphur dioxide; acidic alkyd resins; and a number of salts including sodium sulphite, potassium bisulphate, aluminium chloride, nitrate, and sulphate, lead acetate, and chlorides of zinc, iron, and ammonium. Other condensing agents include zinc and lead dust, zinc oxide;[4] chlorides of zirconium, calcium and tin(ous); bromides of sodium and potassium; aluminium acetate; and the tartrate, citrate, and lactate of titanium.[5]

Reactivity of Various Phenols.—Holmes and Megson [6] have shown that *p*-cresol, phenol, *o*-cresol, *m*-cresol and sym-xylenol react in this order with xylenol the most reactive using trimethylamine as a catalyst.

Constitution of Phenolic Resins.—Condensation with aldehydes occurs at positions para and ortho to the hydroxyl group of the phenol.

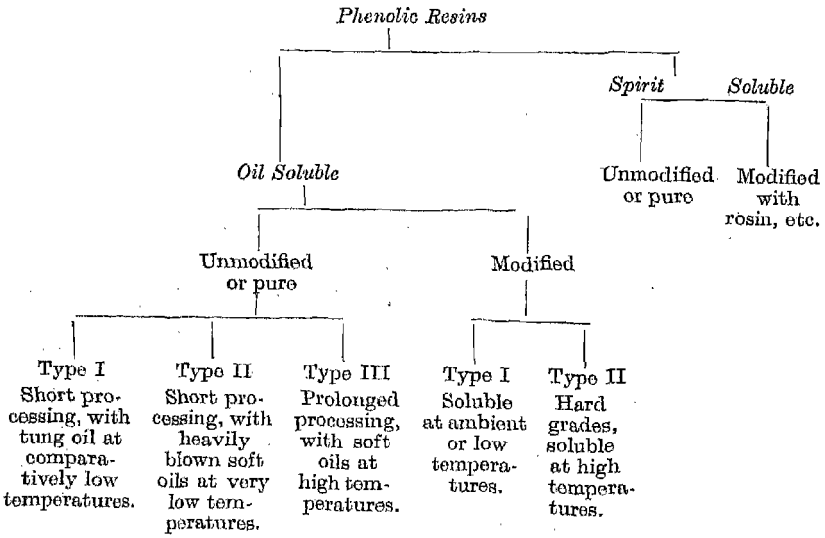
Baekeland considered that the reaction took place in three stages. A product *A* is first formed and this may be liquid or solid. Further condensation yields product *B* which is an insoluble fusible solid. The final product *C*, obtained by heating *B* is an insoluble infusible solid. Many theories have been advanced to account for the constitution of phenol formaldehyde resins but such a discussion is beyond the scope of this book. The foundations for study can be found elsewhere.[7]

Ratio of Constituents and Effect on Resin Properties.—The ratio of formaldehyde to phenol is said to have a marked influence upon the nature of the final product. Ruff[8] states that when the molecular proportion of formaldehyde is greater than the molecular proportion of phenol the resin passes to the *C* stage. When the proportions are reversed the resin is soluble and fusible. Baekeland has also stated that increase of formaldehyde produces infusibility.[9]

Classification of Phenolic Resins

A clear classification of phenolic resins is difficult. Broadly, they may be divided into two types—those which are soluble in drying oils and those which are not. The latter type are soluble in alcohols.

CLASSIFICATION OF PHENOLIC RESINS



The oil-soluble phenolic resins may be further subdivided into the unmodified or pure types, and those which have been modified by the introduction of rosin, ester gum, drying oil components, etc.

The unmodified resins may be specially designed for short processing with hard oils like tung oil at comparatively low temperatures ; for short

processing with heavily blown soft oils at very low temperatures; or for prolonged processing with soft oils like linseed, at or near stand oil-making temperatures. The resins may be noticeably "reactive" as evidenced by considerable frothing, or quietly "reactive" as evidenced by an increase in viscosity alone. The subject of the "reactivity" of phenolic resins, is, however, considered in greater detail subsequently.

The modified oil-soluble resins may be subdivided into two types: those which are readily soluble in drying oils at ambient or low temperatures, and harder grades which need careful cooking at high temperatures to effect solution. The former are usually soluble in aliphatic hydrocarbons and the latter only partly soluble or completely insoluble.

The phenolic resins which are insoluble in or unsuitable for drying oils, but soluble in alcohols, again may be represented by two main types—those which are unmodified and pure, and those which contain large amounts of rosin.

Composition of Oil-soluble Resins.—From the varnish-making point of view only those phenolic resins which are soluble initially or which can be made soluble in oils by subsequent treatment are important.

Oil-soluble resins can be made from the following combinations: 1 . 3 . 5 . iso-propylcresol and formaldehyde, 1 . 3 . 5 . methyl ethyl phenol and formaldehyde, both in the presence of oxalic acid; from furfural and phenols; from tertiary butyl phenol, tertiary amyl phenol, *p*-cyclohexylphenol or *p*-cresol with formaldehyde in the presence of caustic soda; from *m*-cresol or sym-xylenol and acetaldehyde or paraldehyde; from *p*-ethyl phenol and formaldehyde in presence of caustic soda; from cresol or xylenol and formaldehyde with ammonia; from *p*-tertiary heptyl phenol and formaldehyde in presence of caustic soda; and from amyl phenol and formaldehyde in presence of mineral acid.[10] The fractions from crude xylenol are another source for the production of oil-soluble resins when condensed with formaldehyde in the presence of oxalic acid. The fractions cited contain 2 . 4, and 2 . 5 xylenol (b.p. 210°–218° C.); or 3 . 5, 3 . 4, and 2 . 3 . xylenol (b.p. 216°–229° C.); or 3 . 4 . xylenol and 2 . 4 . 6 . trimethyl phenol[11] (b.p. 223°–229° C.). Other phenols used in the manufacture of resins include *p*-cumylphenol, $\alpha\alpha\lambda\lambda$-tetramethylbutyl phenol, *o*- and *p*-chlorophenol, sym-diethyl phenol, *m*-ethoxyphenol, and *m*-hydroxypropyl phenol.[12] Thymol, carvacrol, and *p*-phenylphenol yield resins which dissolve in wood oil on heating. The same author states that resins from phenol, *o*- and *m*-cresol, or the naphthols are insoluble in oils,[13] although Aylsworth claims to have made an oil-soluble resin from *o*-cresol and formaldehyde.[14]

Oil-soluble resins can be made either with acidic or basic catalysts. Acid catalysed resins are sometimes described as Novolaks or resites; alkali catalysed resins are known as resols. Substituted phenols yield resins which are more compatible in oil than resins from straight phenols,[8] and Hönel[15] emphasises that straight chain substituents have a greater influence on oil compatibility than branch chain substituents.

There are also naturally occurring substituted phenols which give excellent varnish making resins. Some are still in the process of assessment but cashew nut shell liquid resins have now definitely established themselves as important resins. They are dealt with as a class in a separate section on page 193.

Reactivity of Phenolic Resins with Drying Oils.—Breuer [16] divides oil soluble phenolic resins into two groups: (*a*) oil-reactive and heat-hardening, and (*b*) non-reactive and non-hardening. This classification is a satisfactory one if the extent of the truth of the description "oil-reactivity" is clearly understood. It is in the first class that the unmodified phenolic resins are found.

Considerable controversy exists as to whether phenol formaldehyde resins react with drying oils on heating. On heating these resins with drying oils, water and formaldehyde are evolved and the mixture increases rapidly in viscosity. The extent of the "reaction" has been measured by determining the amounts of water and formaldehyde evolved in comparison with that from the resin alone; or by following the increase in viscosity of the mix after making some allowance for the natural polymerisation of the resin.[17] "Reactivity" is most evident with oils containing conjugated double bonds, such as wood oil and dehydrated castor oil. Blown oils are also reactive.[17] Bodying occurs also with linseed and perilla oils although to not such a marked degree as with the oils previously mentioned. The speed of polymerisation is, however, greater than that of the natural oil.

There is no disputing that the heat treatment of drying oils, particularly those with conjugated bonds, with certain types of substituted phenolic resins, produces profound physical changes. These are changes which do not occur either with "non-reactive" resins or with the oils alone under the conditions of treatment.

It is a moot point whether these physical changes are the visible signs of a chemical reaction between the resins and the oils or not. Singer asserts that there is a greater reduction in double bond content by heating tung oil or linseed oil with an oil reactive alkyl phenol resin than by heating the oil alone. On these findings, he concludes that a chemical reaction at the double bonds has occurred. His theory is based on the assumption that methyl quinone is formed during the hardening of the resins, and that this reacts with the double bonds.[36]

Heat Hardening.—The other characteristic of these resins is the hardening on heating, and this is evidenced by frothing and an increase in melting-point. Heat hardening appears to be influenced chiefly by the ratio of phenol to formaldehyde in the resin, and Hönel states that reduction of formaldehyde diminishes heat hardening capacity.[15] Hardening improves the chemical resistance.

Incorporation of Phenolic Resins in Drying Oils.—The technique employed in the incorporation of oil-reactive heat-hardening resins in drying oils is practically the same for all resins of this class. They are

used to best advantage with wood oil or similarly constituted oils and the method is to heat the oil alone up to a temperature of 200° C. The resin which has been broken into small pieces is then gradually fed in with constant stirring. The temperature will recede to approximately 180° C. and it should be maintained at this point until the resin has dissolved completely. Failure to provide adequate stirring means that the resin becomes overheated on the bottom of the pot and polymerises rapidly, ultimately yielding an insoluble gelled mass, in addition to promoting unnecessary darkening.

The temperature is then gradually raised to 200° C. Too rapid heating results in excessive frothing which may be difficult to control. The temperature is maintained at 200° C. until the frothing subsides. The mix is then heated slowly to 240° C. when frothing recommences. After prolonged cooking at this temperature the frothing subsides again and cooking is then continued at this temperature or higher until it is deemed that the mix has attained sufficient body. This is usually indicated by a strong string from a cold glass plate. It is probably more essential with this type of varnish than any other to stir continuously throughout the heat treatment. If linseed oil is to be added it is best added as a stand oil after the reaction with the wood oil at 240° C. has subsided, or as a chill back when the resin/wood oil mix has reached sufficient body. If the resin is a mixture of pure phenolic resin and ester gum or modified phenolic, the most convenient method of treatment is to process the pure phenolic with wood oil and to check back with the other resins.

Some types of pure phenolic resin are especially suited for use with linseed or perilla oil alone, but the method of treatment is quite different from that with wood oil. With these oils the oil is heated initially to 200° C. and the resin added as before in small pieces. When it has dissolved and after a preliminary treatment at 200° C. the temperature is raised to 290° C. and maintained until a good body is obtained. This requires a time of half an hour or more depending upon the ratio of resin to oil. These combinations of resin and oil exhibit good drying properties and excellent water resistance.

Shuey has studied the effect of various types of phenol formaldehyde resin on the bodying of oils, especially wood oil. He recorded that the properties of this type of resin vary considerably.[18] Ruckert emphasises that raw wood oil is preferable for use with pure phenolics to polymerised wood oil, by reason of easier dispersion and economy in fuel.[19]

Unmodified xylenol formaldehyde resins are particularly "reactive" with blown or oxydised drying oils and need special care in handling. However, if solution is effected at low temperatures, with constant stirring, oil-resin products are obtained which possess valuable gelling properties.

Hardening of Rosin and Ester Gum with Phenolic Resin.—Pure phenolic resins have the property of hardening rosin and ester gum. One part of Beckacite 1001 and three parts of ester gum after heating together to a

maximum temperature of 250° C. yield a resin paler than the ester gum with a melting-point of 140° C. and acid value of 11·4 (ester gum, m.p. 89° C.). Increasing the ratio of ester gum to Beckacite 1001 (4 : 1) results in much less frothing, giving easier control and a final product with a melting-point of 118° C. and acid value 14·1. The maximum melting-point 148° C. is obtained from a mixture of two parts of ester gum and one part of Beckacite 1001. Similar experiments with rosin showed that the melting-points of the resultant products were generally somewhat lower than the corresponding ester gum mixtures (4 : 1, m.p. 118° C.; 3 : 1, m.p. 135° C.; 2 : 1, m.p. 145° C.) and that the acid values were higher, 134·1, 129·0, and 114·0 respectively. Frothing occurred with the rosin mixtures but was much easier to control. Modified phenolics are obtained by the above means, and the products are quite soluble in drying oils, and compare favourably with proprietary modified phenolics which are claimed to be made by incorporating the modifying agent during the actual manufacture of the base resin. It is not possible to state that the modified phenolics produced by the two different methods behave similarly under all conditions, but there is no doubt that those prepared by heating pure phenolic resins and modifying agents as above often yield results comparable with the other type, with the additional advantage that they are cheaper from the varnish maker's point of view. This contention is supported by American workers.[20]

Properties

Durability.—An outstanding feature of pure phenolics with wood oil is a durability probably surpassed only by that of alkyds. Composition of the resin has an influence on the durability of the resultant varnish, for example, in short oil varnishes a *p*-hydroxydiphenyl resin yields more durable results than an alkali condensed *p*-tertiary butyl phenol. So-called oil reactivity is not necessarily a criterion of durability.[21] Thomas and Marling suggest that phenols may have an anti-oxidant effect upon the ageing of oils which may contribute to the improved durability with linseed oil.[22] The influence upon durability of pure phenolics is so marked that they may be diluted with cheaper resins such as ester gum without serious detriment. Sprinkel claims that pure phenolic-natural resin combinations have better durability than corresponding ester gum combinations.[23] When wood oil is the only oil present durability begins to be lost when the oil-pure phenolic resin ratio falls below two of oil to one of resin. The best proportions are 2½–3 of oil to 1 of resin. Although the greater part of the oil may be wood oil the addition of a little linseed stand oil is an advantage. Improved durability of exterior paints is obtained after fortification with pure phenolic resin.[24] Wood oil-pure phenolic varnishes do not possess exceptional gloss. Varnishes rich in wood oil give hard films but lose gloss on exposure as the proportion of wood oil is increased.[25]

The addition of many resins to alkyds upsets their durability. If care is taken in their incorporation pure phenolic resins may be used with alkyds without detrimental effect upon durability, but with a satisfactory influence upon water and alkali resistance.[26] Phenolic resin modified alkyds are discussed at greater length in the section on modified phenolic resins.

Effect on the Drying of Oils.—The effect of pure phenolic resins upon the dry of oils depends upon certain factors, among which may be included the type of resin, the presence of free phenol, and the method adopted for incorporation into oil. As already stated, certain resins, by heating with linseed oil at high temperatures (290° C.), provide varnishes with outstanding drying properties. Ulrich, however, has reported that the addition of Beckacite 1001 to linseed-wood oil stand oil does not improve the dry,[27] although an improvement in water resistance was noticed. It is known that some phenols retard the dry of linseed oil whilst with wood oil the reverse has been reported.[22] Free phenol may be removed from phenol formaldehyde resins by solvent extraction. Solvents used include benzol, toluol, chlorinated hydrocarbons, benzine, and ether.[28]

Influence on the Webbing of Tung Oil.—An important property of pure phenolics is that they make it possible to produce gas-proof varnishes from wood oil after relatively low temperature treatment. Oil-resin mixtures which are prone to web have this tendency removed if about 10 per cent of the resin is replaced by pure phenolic resin.

Water, Solvent and Chemical Resistance.—Phenolic resins are particularly suitable for the production of water resistant finishes (boat and seaplane varnishes), varnishes for electrical purposes, solvent-resisting varnishes and chemical-resistant varnishes. These varnishes are dealt with in detail elsewhere.

Yellowing.—A defect of some pure phenolic resins is their tendency to yellow on exposure to light and this yellowing usually occurs within a few hours of exposure. Types of resin are available which are practically free from this defect, and these can be used in media for light tints of pigmented enamels if desired. The formation of quinine-like bodies is said to be the cause of after-yellowing, but if substituents are present in positions para to the hydroxyl group these bodies cannot be formed and after-yellowing is prevented.[29] Alternatively a phenolic resin hydrogenated under pressure at an elevated temperature in the presence of a catalyst has been suggested.[30]

Selection of Driers.—Some resins yield precipitates when lead drier is used in the varnish if the temperature of incorporation is too high. Temperatures below 100° C. are recommended for addition of lead-terebine. Pickett notes that manganese and cobalt driers help to maintain lead driers in solution.[31]

Selection of Solvents.—Oil soluble resins based on certain phenols need at least a proportion of strong aromatic solvent in the thinners to

keep a clear varnish. Some varnishes even with these thinners remain slightly opalescent, but this defect, unless very pronounced, is generally ignored. Some resins give star-bright varnishes with white spirit only.

Darkening on Stoving.—All phenolic resins exhibit darkening on stoving and should not be used except in media for dark-coloured enamels or blacks.

Alcohol Soluble Phenolic Resins

Composition.—Another type of pure phenolic resin which is used in important quantities is that produced from the interaction of formaldehyde and phenol or cresol. The products are supplied either in the form of soft sticky resins or as their solutions in certain solvents.

Thermosetting Properties.—They are applied usually by spraying, coating machine or dipping, and dried by stoving at temperatures ranging from 105° C. to 190° C., depending upon the result it is desired to attain. The duration of stoving varies from one to two hours at the lower temperatures to only fifteen minutes at 190° C. Stoving results in hard brittle insoluble films. From a consideration of electrical properties, Kremlevskii has studied the rate of polymerisation of phenol and cresol formaldehyde varnishes at 90°–110° C. Phenol resins polymerised more rapidly than cresol resins in the ratio of 2·2 to 1.[32]

These resins are usually described as the thermosetting alcohol soluble type as distinct from the oil soluble type. Granger states that all phenol formaldehyde resins are soluble in acetone.[13]

Uses

The alcohol soluble thermosetting resin is used extensively as an insulating varnish and as an impregnating solution for a number of materials, including paper, cardboard and wood. Wood has been subjected to low pressures to remove occluded air and then impregnated with solutions of resin in methyl alcohol which is forced in by pressure. After air drying, the temperature is gradually raised to 100° C. when curing takes place. The hardness and strength of the wood are increased as well as the moisture resistance.[33]

Tough glossy finishes for wood, known as cold setting lacquers, are obtained using solutions of phenolic resin in alcohol or suitable solvent, to which an acidic accelerator is added just prior to application. By this method the resin is polymerised to its insoluble state at ordinary temperatures, and the danger of damage to the wood or shrinkage through baking at elevated temperatures is averted. Recent developments involve drying at temperatures slightly above atmospheric, e.g. 110°–120° F., under controlled humidity. This procedure gives a very rapid drying rate without danger of wood distortion. The films obtained have good water resistance and are durable, elastic and have good adhesion. In addition they do not burn easily and are resistant to alcohol and chemicals.[34]

The disadvantage of many of these cold setting lacquers is that often corrosive acidic accelerators have to be handled and mixed with the lacquers just prior to use. Gelation occurs after a few hours at ordinary air temperature, and if the doctored lacquer is not consumed before this stage it becomes a waste product. The great advantage of these lacquers is that several coats of lacquer can be applied as soon as the solvent has disappeared from the previous one. Subsequent light stoving satisfactorily polymerises the heavy multi-coat film.

The catalytic effect of the added acids increases in rough proportion to the concentration of the acid mixture, but in practice only 1 or 2 per cent of concentrated acids are used. The stronger mineral acids are more effective than the weaker or organic ones. Fonrobert[37] has published the results of work conducted with the following acids: oxalic, adipic, uric, sebacic, hydrochloric and phosphoric acids and their mixtures, and in addition, acetic, chloracetic, and sulphuric acids, and organic acid chlorides may be included. Use is also made of a product formed by the interaction of triethanolamine with phthalic or tartaric acids.[38]

A blend of hardenable phenol formaldehyde and urea formaldehyde resins with an acid accelerator has been used for wood impregnation also.[35]

The addition of the usual plasticisers to resins of the above type result in loss of thermosetting properties. Plasticised resins are available which yield tough flexible films on stoving, but it is believed that the plasticising agents are incorporated in the resin at the time of the reaction between the aldehyde and the phenol.

Modified Phenol Formaldehyde Resins

Modified phenolic resins are used in much greater quantities than the pure variety. This is because, except for special types of varnish, the latter is prohibitive in cost. Even after modification with diluents such as rosin the resultant product possesses in good measure some of the characteristics of the basic phenolic resin. Moreover, modified phenolics are often more readily soluble in oils at low temperatures and do not need a complicated heat treatment. They are, apparently, for the most part "unreactive" in that no evolution of formaldehyde or water occurs during the heating process with oils.

Modifying Agents.—Among the modifying agents used natural resins and drying oils are the most important. Insoluble phenolic resins have been fused with rosin or polycoumarone to produce solubility.[1, 28] A resin produced from equimolecular proportions of phenol and formaldehyde, using hydrochloric acid as catalyst, was fused with rosin at 290° C. in the presence of lime to yield a product soluble in oil with an acid value less than 30.[2] An oil soluble resin is made by condensing together phenol and formaldehyde in the presence of zinc compounds. The product is heated with rosin and glycerol until an acid value of less than 20 is

attained.[3] Hydrogenated and polymerised rosins can be used in place of rosin as modifying agents. With polymerised rosin it is not necessary to use so much phenolic condensate to obtain a resin of given hardness. Fifteen per cent of condensate seems to be the limiting amount for optimum properties. Cahall states that a resin with a melting-point of 161° C. can be obtained, by reacting 15 per cent of an alkali condensed *p*-tertiary butyl phenol formaldehyde condensate containing two molecular proportions of formaldehyde to one of phenol, with polymerised rosin. The melting-point only increases to 166° C. if the percentage of condensate is increased to twenty.[40]

Neutralisation of the acidity of rosin modified phenolics with alcohols other than glycerol is another development ripe for exploitation.

A resin soluble in alcohol can be made from a reaction between phenolic resin and rosin.[4] Many cheap modified phenolic resins are available which are soluble in industrial alcohol, and these are characterised by a very high acid value, because of the presence of a predominating amount of rosin. Esterification of a phenol formaldehyde resin with a mixture of linolic acid and rosin yields an oil soluble product.[5] A *p*-cresol formaldehyde resin is dissolved in monolinolein and reacted with phthalic anhydride and tung oil to yield a resin.[6] Oil soluble resinous compounds are produced by heating the condensation products of phenols and formaldehyde, made with sodium acetate as catalyst, with castor or linseed oil.[7] Phenol formaldehyde resin made with oxide, hydroxide, or organic zinc salts as catalyst is heated with a partial ester of glycerol and a higher fatty acid. A resin with an acid value less than 20 is obtained.[8] A resinous composition is made by heating an oil soluble phenolic resin with tung oil. Drying oils and glycerol are then added and the heating continued. Phthalic acid is added finally and the reaction continued.[9]

Another method of producing an alkyd modified phenolic resin is to heat a butyl phenol-formaldehyde resin, phthalic anhydride, glycerol and linseed oil fatty acids together. Linseed oil is added finally and the whole polymerised together at 280° C.[10]

Rosin esters, including glyceryl diabietate and glyceryl triabietate, may be reacted with phenolic resins.[11] Phenol aldehyde condensation product is heated with rosin and tung oil.[12]

An alternative method of incorporating modifying agent is to introduce it during the actual condensation of the phenol and the aldehyde. Modifying agents used include rosin and Manila copal.[13] Rosin has been condensed with crude cresol in the presence of boron fluoride. The product is esterified with glycerol and then reacted with paraformaldehyde.[14]

Unsaturated fatty oils and phenols are heated together in the presence of inorganic basic compounds and the resultant product is condensed with aldehyde. In an example linseed oil and cresol are heated in the presence of lead acetate and the product reacted with formaldehyde.[15]

A phenolic modified alkyd is obtained by heating together phenol, tung oil, phthalic anhydride and glycerol. In this case the resultant product is condensed with formaldehyde with ammonia as catalyst.[16]

Phenol is condensed with excess of formaldehyde in the presence of an A stage oil soluble alkyd.[17] Amyl or butyl phenol, formaldehyde, and rosin are heated under pressure, using zinc acetate as catalyst. The product is esterified finally with glycerol by heating at 240° C. for twelve hours.[18]

Resins of the albertol type can be made, according to Ushakov and Zeltzer, by the following method: 60 parts of formalin (40 per cent soln.), 100 parts cresol, and 50 parts of abietic acid are heated for five hours and the product esterified with 8·5 parts of glycerol (28° Be.) for seven to eight hours at 250°–260° C.[19]

Mixed xylenols, tung oil monoglyceride and formaldehyde are heated together in methyl alcohol, using caustic soda as catalyst. A reaction product formed from diphenylphenol, formaldehyde and glycerol is neutralised by a subsequent reaction with rosin or drying oil fatty acids.[20]

Paraformaldehyde, xylenol, tung oil and triethanolamine have been reacted together.[21]

An oil soluble modified phenolic resin is made from *p*-tertiary amyl phenol by refluxing it with a methyl alcohol-free aqueous formaldehyde solution and melamine.[39]

Cresol formaldehyde resins modified with aniline provide oil soluble products with pronounced bodying power, especially with blown drying oils.

Mechanism of the Reaction between Phenolic Resins and Rosin.—Sleightholme has suggested three possible types of reaction which might occur when phenol formaldehyde resins are modified with rosin.[22] A reaction may occur between alcoholic groups and abietic acid yielding oil soluble esters; a reaction may occur between alcoholic groups and the double bonds of abietic acid, or the carboxyl group of the abietic acid may react with the phenolic hydroxyl.

The Common Modifying Agents.—Oil soluble modified phenolic resins, which are readily available on the market, include those containing the following modifying agents: rosin, ester gum, natural copals, masticated copal, drying oils and alkyds.

Incorporation of Modified Phenolic Resins in Drying Oils.—The method of incorporation of modified phenolic resins in varnishes varies considerably, and usually the melting-point of the resin is a useful criterion of the treatment necessary. Resins with low melting-points (115°–120° C.) are often readily soluble in petroleum hydrocarbons or drying oils without heating. It is possible to prepare cold solutions of resin in white spirit and to blend these solutions with stand oil and driers to produce varnishes and media. Alternatively, the resin may be dissolved in the oil at the minimum temperature to effect solution. Sleightholme,[22]

however, recommends high temperature treatment of oil and resin mixtures, for the induced interesterification is believed to improve stability and durability. Hard modified resins of higher melting-point are not soluble in white spirit and often require turpentine or turpentine reinforced with aromatic thinners to effect a solution. Neither are they compatible with drying oils without heat treatment. Ease of compatibility with drying oils diminishes with increased polymerisation of the oil. Some hard resins cannot be used satisfactorily with highly polymerised oils when the oil-resin ratio is greater than 1 : 1. The best method of making varnishes from hard phenolic resins is to heat all the resin with not more than an equal part of oil to a minimum temperature of 260°–270° C. If the oils to be used include ordinary unbodied refined linseed oil, this should be used first in preference to the stand oils. When the temperature of the oil-resin mix has been maintained at the minimum temperature for ten minutes a drop is removed and placed on a glass plate. If it remains clear further additions of oil may be made, taking care to avoid excessive additions which will cause turbidity or which will result in substantial temperature drop. While the oil is being added the mix should be maintained over a strong fire to avoid temperature fluctuations, and this object may be assisted by a preliminary heating of the oil before addition. If the mix is caused to go turbid by ignoring the above warnings it may take an unnecessarily long cooking at high temperature to produce clarity again or, in exceptional cases, it may be impossible to remove the turbidity.

After the final addition of oil and the maintenance at the minimum temperature for about ten minutes after the mix has proved to be clear on glass, a sample is tested for solubility in white spirit. A solution containing an excess of white spirit (1 part mix, 2 parts white spirit) is prepared by warming. The solution is cooled. If on cooling turbidity appears the cooking of the mix is continued until a further solubility test shows it to be absent. Pickett [23] has commented upon the effect of high temperatures in cooking modified phenolic resins and oil with reference to petroleum tolerance.

As with pure phenolic resins the modified type shows up to best advantage with wood oil. Some modified phenolics have a strong peptising action on polymerised wood oil but the strength of this influence varies considerably with different types of resin. According to Fonrobert, Holdt and Wilborn,[24] two types of treatment are used. The German method consists in bodying the wood oil alone at 280° C., adding the resin, and cooking just long enough to effect solution. The American method consists in heating the wood oil and resin at 285° C. Products with differing properties are obtained. The German method gives paler and harder varnishes with less skinning tendency, lower viscosity, and better flow. The American method gives more resistant varnishes, especially to hot water and alkali. In addition, they show less tendency to rivel on stoving and are more gas proof. It is the Author's

experience that improved durability is obtained by the American method. Buser asserts that high phenolic resins and wood oil in the ratio of one part of resin to three of oil require a minimum heat treatment of fifty minutes at 245° C.[25] The effect of cooking temperature on the physical properties of a phenolic resin-ester gum-wood oil varnish has been studied.[26] Varnishes were cooked to the same viscosity over a temperature range 230°–290° C. Except for the varnish made at 275° C., which had lower tensile strength and poor durability, there were no differences in physical properties. The effect of viscosity on skinning was also studied. With varnishes made at 260° C. more skinning was evident at the higher viscosities.

Incorporation of Phenolic Resins with Alkyds.—Phenol-formaldehyde-alkyd combinations need special care in determining manufacturing details. These combinations are readily available on the market and methods of manufacture have been indicated already. After preparation of an alkyd resin not more than a few per cent of "reactive" phenolic resin (10 per cent) can be incorporated satisfactorily by heating. Considerable bodying occurs, yielding a product which takes an excessive amount of thinners to reduce it to workable viscosity. In addition, a product with extremely poor drying properties may result. Alkyds incorporating wood oil or its fatty acids show an even more marked bodying with phenolic resins. Introduction of some strong aromatic solvent may be necessary to obtain a good solution. These highly bodied products may gel on storage.

Cold blends of alkyd and pure phenolic-wood oil varnishes rarely yield satisfactory results, and the relative proportion of the two ingredients is another important factor. This can be determined only by experiment. Bad combinations usually result in varnishes with inferior dry—worse than that of either ingredient. This inhibition of dry is also observed frequently when phenolic varnishes are used as undercoating varnishes for alkyds. Probably the most satisfactory method of modifying a phenolic resin with alkyd is to prepare a phenolic resin-wood oil combination in the normal way and to check back at 250° C. approximately with unthinned alkyd resin.

Properties

Most modified phenolics are more readily soluble in oils and thinners than the pure type. It is rare to encounter varnishes or media n which thinners other than white spirit have been used. Turpentine may be added but naphtha is an unnecessary addition. Modified phenolics do not show the same yellowing tendency as the pure phenolics, but this may be attributed, in part at least, to the fact of dilution. Modified phenolics for oil varnishes are believed to contain between 15 and 35 per cent of pure phenolic resin.

Media or varnishes which are subject to extreme dilution with thinners to accommodate certain methods of application are made best

on modified phenolic resins. The complex product of pure phenolic resin and wood oil is apt to be unstable under these conditions.

Uses

Although not so powerful in their effect as pure phenolic resins the modified type is a useful reinforcing agent for the cheaper varnish resins, including rosin, rosin ester, limed rosin, zinc resinate, copal ester and natural copal. Zinc resinate in combination with phenolic resin gives superior varnishes to corresponding mixtures of ester gum or limed rosin.[27] Modified phenolics with wood oil give varnishes of good durability. These are a marked improvement on the old natural copal varnishes. Natural copals with a little modified phenolic resin show appreciable improvement in durability. Very durable varnishes can be made from alkyd-phenolic resin-wood oil combinations.

Other uses for modified phenolic resins include water, acid, alkali and petrol resistant varnishes, paint and enamel media, aluminium and bronze media, rubbing varnishes and printing varnishes.

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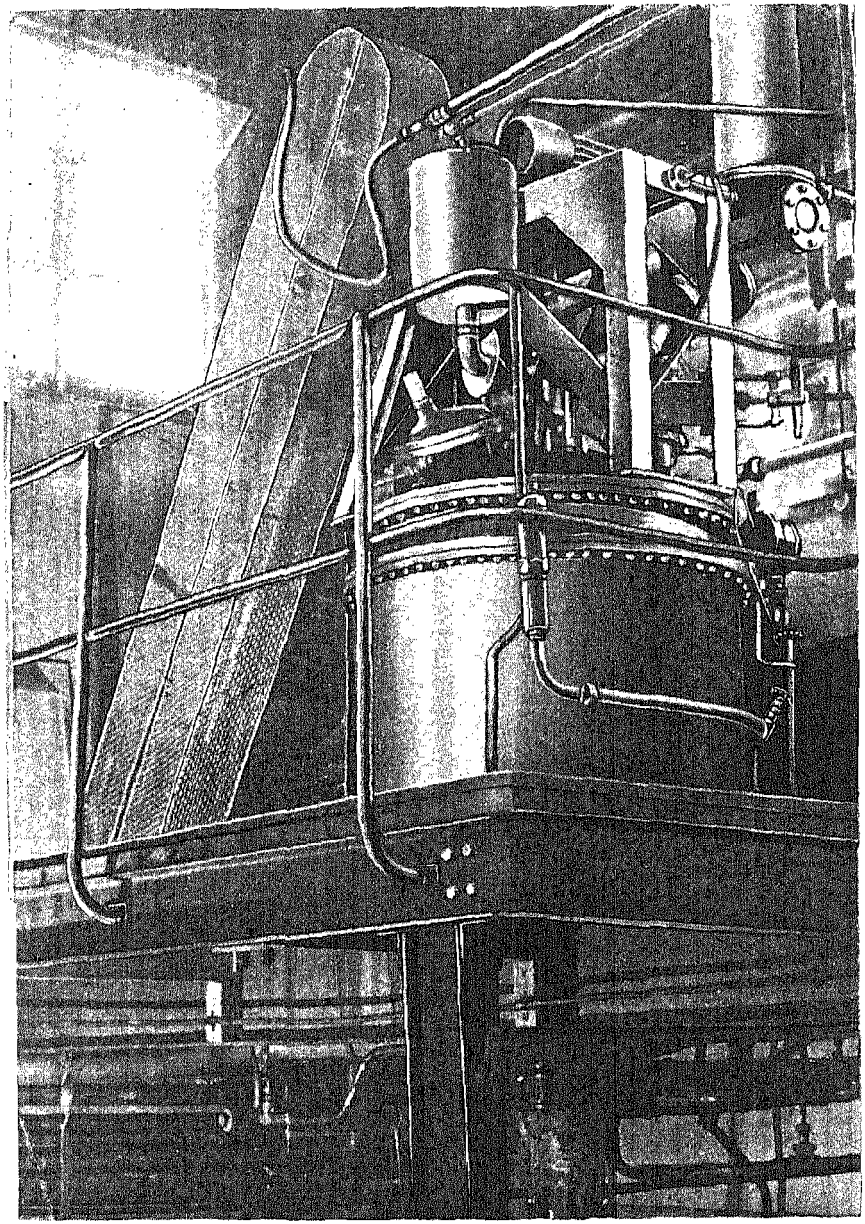

PHENOLIC RESIN DIGESTER

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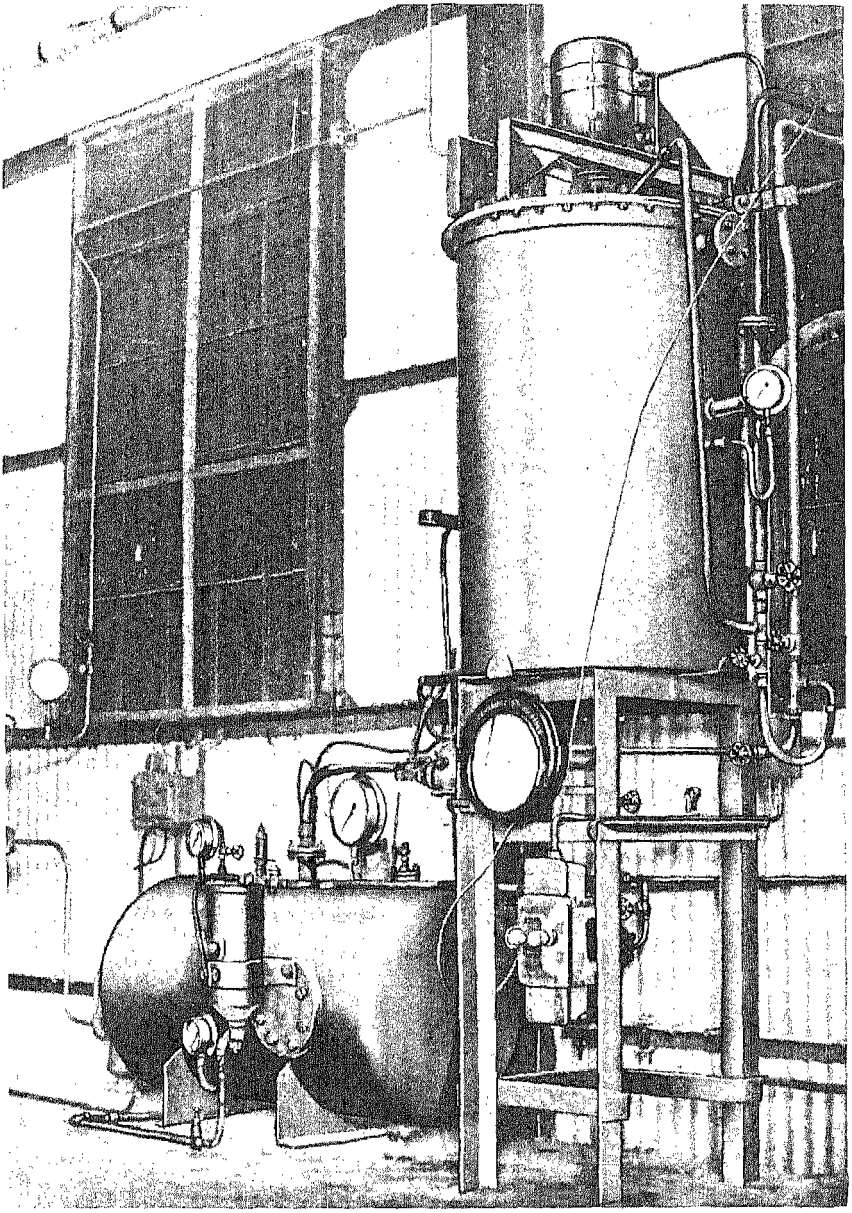

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Cashew Nutshell Liquid Resins

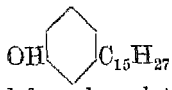
Cashew nutshell liquid is a typical example of a naturally occurring "vegetable oil" containing a substantial proportion of a substituted phenol. The "oil," if it can be described as such, differs from the usual vegetable or animal oils in that its primary constituent is phenolic in character, whereas the latter oils are essentially triglycerides. Probably the most confusing thing about cashew liquid is that it is not derived from the kernel of the nut, which would seem to be its most likely location, but from the shell around the kernel. The kernel itself is edible and is consumed in large quantities both in America and India.

The nuts are indigenous to India (southern half), America, Brazil, and South Africa, although India is the most important source. The extraction and subsequent manipulation of the nutshell liquid are

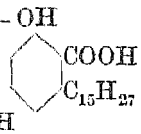
covered by a number of American-held patents. The resins are, however, in the process of development and production in the United Kingdom also.

The liquid is not easy to obtain from the nuts, and the first used method was to subject the nutshells to a temperature sufficiently high to cause destruction and charring of the shell. This, in turn, enables the occluded liquid to be forced out. The other method is an extraction using hot oil.

The nutshell liquid as it occurs naturally, consists of about 10 per cent of cardol—a dihydric phenol with a linear side chain containing two unsaturated bonds, and formula :— with 90 per cent of

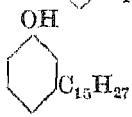


anacardic acid :—



This acid decarboxylates on heating to yield,

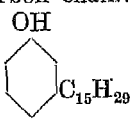
anacardol :—



Preliminary investigations were conducted on the oily product obtained by cold solvent extraction. It is not surprising, therefore, now that the composition of the material is known more intimately, that Patel [3] found that the product obtained by the normal heat treatment differed from the oil obtained by solvent extraction ; the anacardic acid content of the former was only 16 per cent against over 90 per cent for the extracted oil.

The commercial liquid, as obtained by heat treatment, is of a dark reddish-brown colour and is quite viscous. An important constituent, cardanol, obtained from it by steam distillation, is a monohydric phenol substituted in the meta position by an unsaturated hydrocarbon chain.

This has been assigned the formula :— and resembles anacardol except that only one unsaturated bond occurs in the side chain. The mechanism for this transformation is not, as yet, fully understood. It is the presence of the hydrocarbon chain of the phenol which confers on the resins made from it their unusual properties.



The crude liquid obtained from the shells undergoes careful purification before it is used for any type of resinous product. Mineral salts are precipitated by treatment with sulphuric acid, or similar reagents, and the resultant insoluble matter removed by filtration. This chemical treatment also promotes some decomposition of an organic sulphur compound, as evidenced by evolution of hydrogen sulphide.

The changes which result from this chemical treatment are not profound as the figures facing, given by Harvey and Caplan,[1] indicate.

Raw cashew shell liquid has a definite vesicant action, but chemical

treatment greatly reduces this, and the action seems to be associated with sulphur compounds which suffer degradation during the above treatment.

Downing and Gurney have studied the physiological effects of raw cashew nutshell liquid, and report that dermatitis associated with skin eruptions, is caused by contact. It is recommended that rubber gloves are used when handling the nuts and that workers' clothes are subjected to a hot-ironing daily.[6]

It seems unlikely, however, that skin irritation or more extensive damage, should occur in handling the ultimate resins, because of the possible neutralising processes, especially high temperature treatment, involved in the preparation of these resins. But it is wise for the varnish maker to use them with care until the available knowledge on the subject is greater. Hale of the U.S. Public Health Service has shown commercial nutshell liquid to be non-toxic to white mice.[2]

TABLE SHOWING THE EFFECT OF CHEMICAL TREATMENT ON CRUDE CASHEW LIQUID

	I.V. (Wijs)	R.I. 20° C. Average	Acetyl Value	S.G. $\frac{25°}{15°}$ C.	S.V.	Vis. Centipoises 25° C.
Before treatment	269	1·5160	173	0·958	19·6	400
After treatment	254	1·5215	156	0·960	29·7	435

The treated cashew liquid or cardanol can be reacted with aldehydes, and the reaction is hastened by the usual catalysts. Ammonia is just one example of a suitable catalyst. Aldehydes which have been used successfully in resin manufacture are formaldehyde and furfuraldehyde.

Alternatively the cashew liquid may be polymerised by heat treatment alone or with the assistance of catalysts. Suitable polymerisation catalysts are sulphuric acid and the alkyl sulphates.

A patent covering this polymerisation treatment cites the use of at least 2 per cent of diethyl sulphate or other suitable mono- or dialkyl sulphate with or without sulphuric acid ; and the mixed cashew nutshell liquid and reagent is heated at 160° C. to effect the necessary polymerisation. This treatment obviates the necessity of acid purification of the crude liquid mentioned above, for precipitation of the contaminating metals and polymerisation occur simultaneously.[5]

The non-volatile residue from cashew nutshell liquid after distillation, whether ordinary or steam, can be polymerised in a similar manner by treatment with dialkyl sulphate. The product is valuable as an electrical insulator.[8] This is equally true of the distillate also (cardanol), which undergoes polymerisation similarly. The polermised products react readily with aldehydes, and in particular paraformaldehyde, which is used with them to yield rapid setting compounds, even at ordinary atmospheric temperature. The reaction between cashew nutshell liquid

and paraformaldehyde is facilitated by the presence of a benzeneshlphonic acid and a benzenesulphonyl chloride as catalysts.[9]

For certain purposes the commercial shell liquid is distilled, as described above, to give an amber liquid of fairly constant boiling-point which consists substantially of cardanol.[10] The physical constants of this very valuable distillate are worth recording : sp. gr. 0·930 $\frac{20°}{4°}$ C. ; b.-pt. 360° C. or 225° C. at 10 mm. ; m.-pt. $< -20°$ C. ; and n_D^{25} 1·5113. Whilst this distillate does not polymerise so readily as the parent liquid it has special uses, and as explained already is polymerised by the sulphate method. The formaldehyde condensation product of the distillate—a very useful resin—cures slower than a similar product from the undistilled liquid.

The cashew nutshell liquid can be etherified to form the propyl, butyl, or amyl ethers, etc. ; the volatile ether is removed by destructive distillation and the residue is condensed with an aldehyde to form a resin.[4] Cashew nutshell liquid or cardanol can be condensed with other phenols in the presence of sulphuric acid, and the products further treated with aldehydes to give soluble oil varnish resins.[10] Alternatively it is claimed that the nutshell liquid-phenol product can be used as a resin without further treatment.[11] Mixed ether-esters are prepared by reacting, either cashew nutshell liquid or cardanol derived from it, with alkyl chlorides such as amyl chloride, under alkaline conditions. The products are said to be suitable for use in varnishes.[7]

Cashew nutshell liquid resins are thermosetting, whether of the polymerised, the aldehyde condensation, or the polymerised-aldehyde condensation types. The films are characterised by a toughness and flexibility not usually associated with phenolic-aldehyde resins. They possess, in addition, good stability at elevated temperatures, and very good solvent and chemical resistance when completely cured. The cashew nutshell liquid-aldehyde resins are especially interesting because of their excellent drying oil and aliphatic hydrocarbon compatibility. The aldehyde condensation products, either alone or in conjunction with drying oils and/or other modifying agents, provide excellent varnishes for electrical purposes. Other applications for cashew resins include media and fillers for brake linings ; mixtures with rubber to improve solvent resistance ; binding agents for bonded paper ; water resistant plywood adhesives ; rapid setting cable compounds ; and mica cements. Morgan[12] has given an excellent review of the production and properties of cashew nutshell liquid resins.

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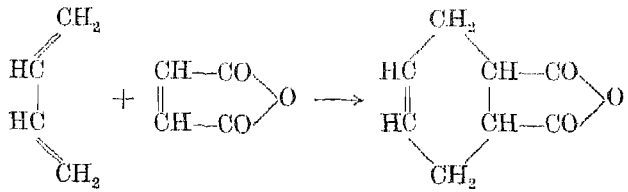
Maleic Resins

Of all the raw materials used in the manufacture of resinous compositions maleic acid or its anhydride is one of the most important. In addition to its use in the production of alkyd resins described elsewhere, it undergoes many other valuable reactions. It reacts with compounds like butadiene according to the Diels and Alder synthesis, with α-methyl pyrrole; with terpenes; with cineole, with unsaturated vegetable oils or their acids; or with vinyl acetate and styrene.

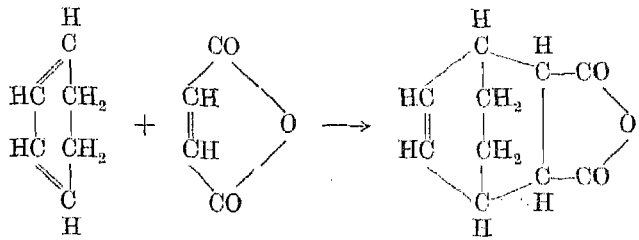
Diels and Alder Synthesis

The Diels and Alder synthesis is important. It is the reaction between conjugated double bonds and the double bond of an αβ-enal grouping. A conjugated double bond (—C=CH—CH=C—) in a compound like butadiene reacts with the αβ-enal grouping (—C=C—$\overset{\overset{\displaystyle O}{\|}}{C}$—) of maleic anhydride.

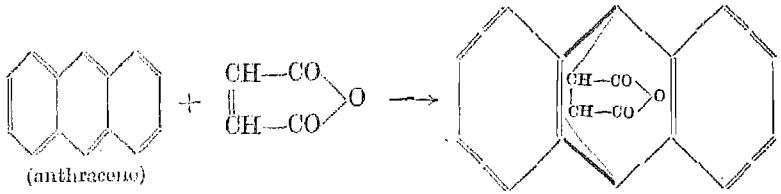


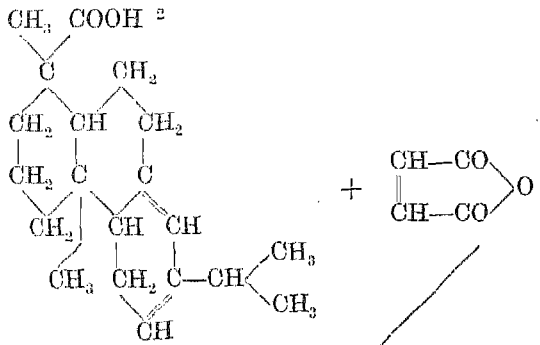
(butadiene)

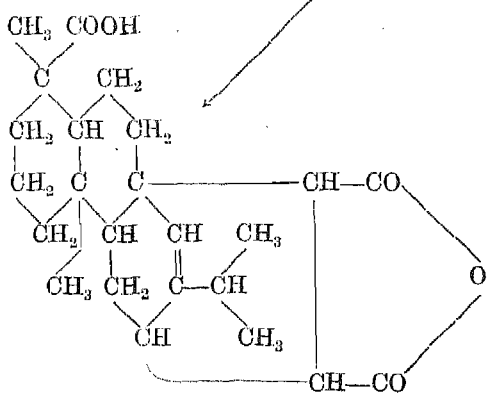
Compounds containing the αβ-enal grouping include aldehydes like acrolein and crotonaldehyde; anhydrides like maleic, itaconic or citraconic anhydrides; quinone and cyclopentadienone. Reactive conjugated double bonds are present in butadiene, myrcene, isoprene, dimethylbutadiene, anthracene, α-phellandrene, α-terpinene, cyclopentadiene, cyclohexadiene, furan, wood oil and possibly in rosin.



(cyclohexadiene)

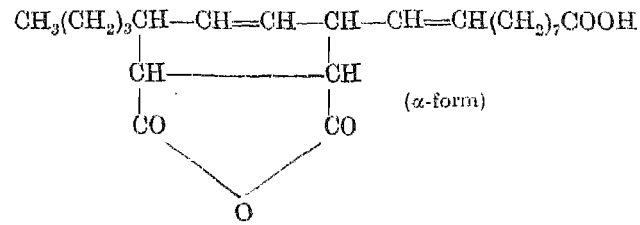




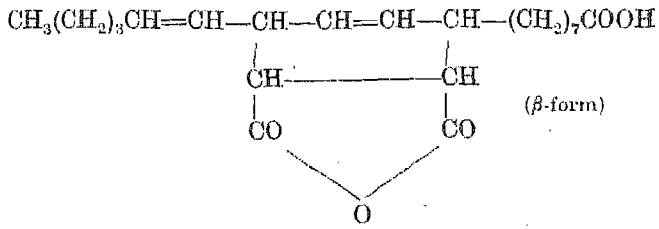


Other constitutional formulæ have been suggested for abietic acid [1] and the presence of conjugated double bonds seems to be somewhat controversial.[2]

From wood oil products of the types shown below are obtained, depending upon whether reaction has occurred between maleic anhydride and the α or β-elaeostearic groupings.



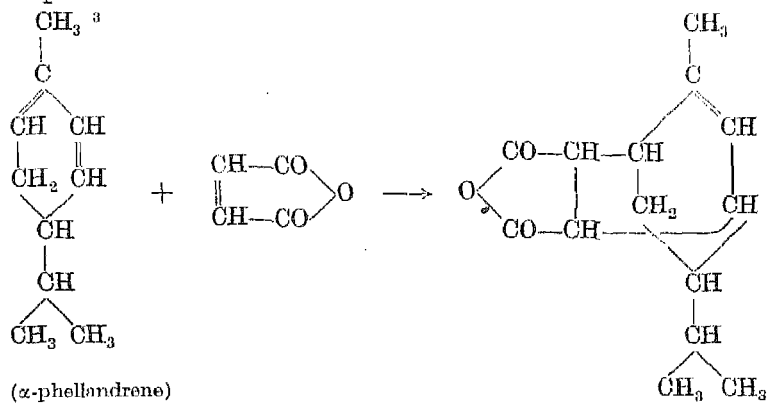
(α-form)



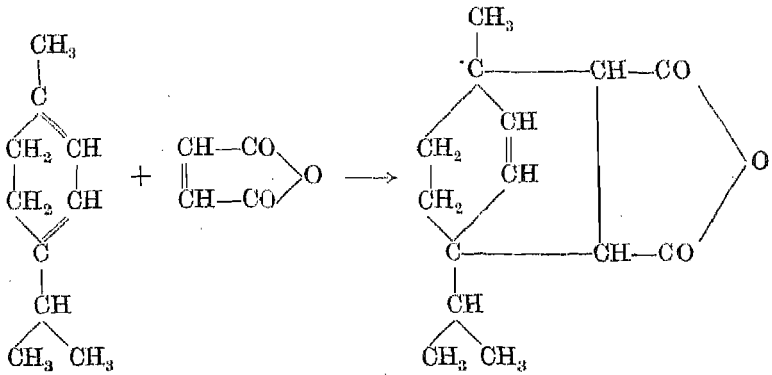
(β-form)

The Reaction between Maleic Anhydride and Terpenes

Terpenes with no conjugated double bonds react with maleic anhydride. These terpenes include α and β-pinenes, terpinolene, *d* and *l*-limonenes and dipentene.



(α-phellandrene)



(α-terpinene).

Varnish Constituents

According to Ensor and Little non-conjugated monocyclic terpenes react with maleic anhydride at high temperatures, yielding an interpolymer of the terpene and the anhydride, and a monomeric addition product following hydrogen migration. The presence of a trace of mineral acid promotes a normal Diels-Alder reaction.[57]

Resinous Products from Maleic Anhydride Reactions

The reaction product from butadiene and maleic anhydride which is cis-Δ4-tetrahydro-*o*-phthalic anhydride, on esterification with glycerol yields a resin.[4] The dibasic anhydrides derived from the dienes present in crude benzol, on their treatment with maleic anhydride are other suitable raw materials for resin manufacture.[5] A non-volatile resinous material is obtained from the interaction of α-phellandrene and maleic anhydride.[6] Similarly, a resin is obtained from α-terpinene and maleic anhydride. A resinous product, suitable for use in varnishes is made by heating maleic anhydride, maleic acid or fumaric acid with excess of α-terpinene at 150°–200° C. α-Terpinene is reacted with maleic anhydride and the product reacted further with glycerol to form a material suitable for use in varnishes. Terpinene-maleic anhydride products may be esterified with monohydric alcohols also. A soft resin soluble in acetone, butyl acetate, or toluene, is made by esterifying the terpinene-maleic anhydride product with glycol. If glycerol replaces glycol a hard resin results.[7] After condensation of maleic anhydride with anthracene, the product is heated with glycerol or glycol.[8] A pale resinous wax is obtained by reacting maleic anhydride and cineole at 140° C. in presence of zinc chloride.[9]

A soft yellow resin is obtained by heating α-pinene and maleic anhydride at 170° C. under pressure. The resin may be esterified with polyhydric alcohols. *p*-Toluene sulphonic acid is a useful catalyst for this reaction. It is believed that the function of the catalyst may be to convert the non-conjugated double bonds into the conjugated type. A pinene-maleic anhydride product is reacted further with a polyhydric alcohol and an organic carboxylic acid.[10]

The dipentene and maleic anhydride reaction product is a resin. It may be esterified with an alcohol. Dipentene-maleic anhydride is reacted with a polyhydric alcohol and an organic carboxylic acid.[11]

A flexible resin is obtained by heating the product of reaction of limonene and maleic anhydride with tetraethylene glycol for one hour at 200°–250° C.[12] Hultzsch claims that satisfactory varnish resins are derived from maleic anhydride and turpentine.[13] Condensation of a terpenic body with maleic anhydride is effected by bringing the anhydride vapours into contact with the terpene at a high temperature.[14]

Bevan records that the reaction between conjugated unsaturated terpene hydrocarbons and maleic anhydride takes place at low temperatures with evolution of heat, in contrast to the reaction with

non-conjugated terpenes which need higher temperatures.[15] The anhydride products obtained from terpenes and maleic anhydride are valuable constituents of alkyd resins, in whose composition they may replace, wholly or in part, the phthalic anhydride. Alkyds derived from terpene-maleic anhydride bases are claimed to be harder, and to have better white spirit and oil compatibility than similar alkyds on a phthalic anhydride base.[15] Littmann states that such alkyds have high melting-points and that they have a beneficial influence on the speed of dry of mixtures with drying oils.[16]

A pale waxy resin is obtained from the condensation of terpineol with maleic anhydride. Such resins may be used as plasticisers for nitrocellulose. It is probable that the tertiary hydroxyl group of the terpineol undergoes esterification simultaneously with the addition reaction.[17]

A high boiling diterpene, obtained from the acid treatment of α-phellandrene, is condensed at 200°–215° C. for three hours with maleic anhydride to yield a resin.[18] The resins thus obtained may be esterified with alcohols. The glycol esters of polyterpene-maleic anhydride resins are heat convertible. Glycol esters of monoterpene-maleic anhydride resins are not heat convertible.[19]

Resins are produced from the interaction of cuprene, maleic anhydride and polyhydric alcohols. Cuprene is prepared by passing acetylene (C_2H_2) over powdered copper at 200°–260° C.[20] Isoprene, maleic anhydride, α and β-elaeostearic acid, and wood oil are reacted together, and the product reacted further with alcohols such as glycol, glycerol, polyglycerol, mannitol or pentaerythritol.[20]

Resins suitable for coating wood and metal are prepared from the reaction products of maleic acid and di-olefines.[21]

Rosin-Maleic Anhydride Resins

The reaction products obtained from maleic anhydride and rosin, or products allied to rosin constituents, are the most important from the varnish maker's point of view. Rosin condensation products may be made in several ways. Rosin will react directly with maleic anhydride on heating at 100°–200° C., and the products are esterified with alcohols to form resins.[22] The resins usually contain about 12 per cent maleic anhydride based on the weight of rosin. Esterification of the abietic acid-maleic anhydride products with glycerol is stated to be liable to cause rapid gelation.[23] Other resins derived from rosin may be used in place of rosin for this reaction, and such resins include polymerised rosin, ester gum, and rosin modified alkyds or phenol formaldehyde resins. Methyl or ethyl abietates may also be used in place of rosin.[24]

In making maleic resins from polymerised rosin in the place of ordinary rosin special practical details must be observed. Since part of the normal unsaturation of ordinary rosin has been involved in polymerisation less

maleic anhydride can combine with polymerised rosin. Cahall suggests that the amount of anhydride should be limited to 12 parts for every 100 parts of polymerised rosin.[60] The actual method to be adopted consists in reacting together the polymerised rosin and maleic anhydride at 180°–200° C. The glycerol is then introduced on a rising temperature which is maintained at 270°–275° C. until esterification is complete. In preparing esterified resins by the simultaneous reaction between polymerised rosin, maleic anhydride, and glycerol, the anhydride should not exceed 9 parts to 100 parts of rosin, if gelation is to be avoided.

Rosin and maleic anhydride may be reacted together by refluxing for four and a half hours in *o*-dichlorobenzene. The acidity of resins produced either by direct reaction or in solution, can be reduced by subsequent high temperature treatment in the presence of zinc chloride.[25]

It has been indicated already, but is worth emphasising that the rosin may be esterified with glycerol before conducting the reaction with maleic anhydride.

Glycerol may be partially esterified with maleic acid and the product reacted further with rosin. Details of a two-stage process involving a preliminary reaction between glycerol and maleic anhydride, followed by treatment with rosin, are given in a recent patent of Reichhold Chemicals.[59] The advantages claimed for this process are an economy in maleic anhydride and a paler product.

Maleic anhydride (2070 lb.) is reacted at a temperature below 170° C. with glycerol (3427 lb.) in a glass-lined vessel. An excess of glycerol is used to prevent gelation. When an acid value of about 30 or less is attained, gum rosin (23,000 lb.) is added slowly and the mixture heated further at 230°–240° C. After treatment by application of a vacuum a resin is obtained with a m.pt. of 115°–125° C. Rosin, maleic anhydride and glycerol may be reacted simultaneously.[26]

Alcohols other than glycerol are used to produce rosin-maleic resins of low acidity, and in this respect pentaerythritol has received special attention. Methyl alcohol has also been included in patented processes.

The low molecular weight alcohols give rosin-maleic esters which are generally soft and of low melting-point. The glycerol ester is probably the first of the series which is useful as a varnish resin, although the ethylene glycol ester is used to some extent in nitrocellulose lacquers.

When pentaerythritol is used as the esterifying alcohol, the maleic anhydride content of the rosin-anhydride complex must be reduced to about 8 per cent in order to avoid insolubility.[61]

The pentaerythritol ester has better water resistance than the glycerol product and gives better drying varnishes. The mannitol ester gives even more marked improvements in properties.

Maleic resins with low maleic anhydride content, but high melting-point are possible.[23]

A resin is obtained by reacting abietic acid, maleic anhydride and α-terpinene together.[27] A compound containing an abietyl radical,

α-pinene and maleic anhydride are reacted together to yield a resin. This may be reacted further with an alcohol.[28]

A compound containing an abietyl radical, a terpene boiling between 170° and 178° C. containing dipentene, and maleic anhydride are reacted to yield a resin.[29]

An unsaturated rosin compound such as an ester of abietic acid reacts with maleic anhydride, and the product is treated with hydrogen to reduce unsaturation. By using hydrogenated abietyl alcohol for reaction with maleic anhydride a product is obtained which is more resistant to yellowing on exposure than a similar product based on non-hydrogenated abietyl alcohol.[30]

Resins other than rosin or rosin modified compounds which react with maleic anhydride similarly to rosin, include damar, mastic, and yellow accroides.

Under certain conditions it appears also that run natural copals may be used in place of rosin.[31]

Fumaric acid also reacts with rosin at 220° C. The resin obtained has a higher melting-point than that from maleic acid.[26]

The methyl or ethyl esters of abietic or pimaric acids are heated with maleic anhydride. The reaction product is then hydrogenated at high pressure (1,500–5,000 lb. per square inch), in the presence of an active base metal catalyst, and the product of hydrogenation esterified with a suitable alcohol.[58]

Properties and Uses

Colour Retention.—The popularity of maleic resins based on the interaction of rosin or its allied products with maleic anhydride, may be attributed mainly to one property; that of colour retention both on exposure and on heating. For this reason maleic resins are used in non-yellowing white or tinted white enamel media or in stoving media or lacquers, in conjunction with stand oils, or with alkyds. They will be found, therefore, in silver stoving varnishes for tinplate or in white stoving refrigerator enamels.

Melting-Point.—The resins themselves can be obtained in hard grades. The melting-points of the resins vary over a considerable range, for example, from 85°–130° C. approximately.

Solubility.—The solubility of maleic resins varies with type, but in preparing straight solutions in solvents it is preferable to use stronger solvents than white spirit. Turpentine, and aromatic hydrocarbons or mixtures of these are recommended. A blend of white spirit and aromatic hydrocarbon may be used. The addition of a small proportion of alcohol is sometimes claimed to be advantageous in effecting solution.

Preparation of Solutions. (*a*) *In Solvents.*—Such solutions may be obtained either by cold churning with the solvent or by melting the resin and thinning.

(*b*) *In Oils.*—When used with drying oils some resins give clear stable solutions without elaborate heat treatment. Generally, however, it is advisable to cook the resin and oil together at 260° C. or higher as in the case of hard modified phenolics. The resin should be heated first with unbodied oil, if the formulation includes this, or with not more than an equal part of stand oil if this is used. When a clear bead from the mix is obtained on cooling, the rest of the stand oil may be added slowly, followed by further treatment to effect solution. When all the oil has been added, the mix should be maintained at 260° C. until it is soluble in twice its own volume of white spirit. Thus, by correct cooking procedure varnishes may be produced which can be thinned entirely with white spirit.

Incorporation of maleic resin with an alkyd resin is best effected by a similar heat treatment to that used for stand oil mixtures.

Effect on Webbing.—When a varnish contains a predominating amount of wood oil or dehydrated castor oil, it is very difficult to obtain a product free from webbing or frosting tendencies. This applies also to the treatment of maleic resins and alkyds containing these oils. The best method to avoid this difficulty is to use in conjunction with the maleic resin about one-tenth of its own weight of pure reactive phenolic resin. This small addition is normally sufficient to prevent webbing and frosting without introducing any substantial yellowing tendency. It should be observed, however, that introduction of pure phenolic resins to alkyds causes excessive stoutening and may cause inhibition of dry. Sleightholme [32] records that the harder types of maleic resins gel rapidly when heated at 290° C. with wood oil, and further, that prolonged heating of the resins at temperatures above 260° C. induces inferior drying properties.

Stability.—Substantial stoutening of pigmented short oil varnishes based on hard maleic resins even with inert pigments is reported by Fonrobert.[33]

Alkali Resistance.—The poor alkali resistance of maleic resins is caused by the presence of maleic esters in the resin complex, in contrast with the abietic esters which have better stability.[23]

Taste and Odour.—Resins yielding tasteless and odourless films are prepared from maleic acid, rosin and a straight chain hexahydric alcohol. The hexahydric alcohol cannot be replaced by glycerol except by forfeiture of the above properties.[34]

Other Properties.—The electrical properties of maleic resins are stated to be good, which permits their use in insulating compositions. Maleic resins may be used also in nitrocellulose lacquers.

Reaction Products of Maleic Anhydride and Unsaturated Oils

The products from maleic anhydride and unsaturated vegetable oils have attracted considerable attention, although, as yet, mainly academic. As might be anticipated the most popular oil for submitting to this type of reaction is wood oil. With this, a reaction occurs at temperatures

in excess of 125° C., to yield a product with vastly different properties from those of the original oil.[35] The product dries slower than untreated oil but has less tendency to web or frost and polymerises at a much slower rate on heating. The acidic product from maleic anhydride and wood oil can be esterified with polyhydric alcohols, but the procedure is difficult and the resultant product of questionable value.[36]

However, a protected process describes the reaction of maleic anhydride with a substance containing the elaeostearic acid radical. The resultant product is esterified with glycerol to yield a heat convertible resin. An A stage resin of this type is claimed to be soluble in naphtha and miscible with warm vegetable oils.[37] A resin suitable for use with nitrocellulose is derived from the interaction of maleic anhydride-wood oil compound, oxalic acid and diethylene glycol.[38]

Morrell and Samuels and others have studied the reaction between maleic anhydride with both the α and β-modifications of elaeostearic triglyceride. Divergence of properties are apparent between the two elaeostearic compounds. β-elaeostearin-maleic anhydride compound is a viscous oil soluble in aromatic hydrocarbons, turpentine and acetone. It can be stoved to give hard solvent resistant films with absence of webbing or frosting, or it can be air dried. The α-elaeostearin-maleic anhydride compound has poor drying properties even on stoving and has poor resistance to solvents.[39]

Reduction of frosting tendency occurs as the percentage of maleic anhydride in the oil-anhydride product increases.[36]

Dehydrated castor oil may be reacted with maleic anhydride, through its unsaturated linkages or compounds may be obtained by the interaction of maleic anhydride and the hydroxyl group of ordinary castor oil.[40]

Prolonged heating of castor oil at high temperatures in the presence of a catalyst induces the formation of conjugated double bonds and eliminates the hydroxyl groups. A flexible resin is obtained from this oil by treatment with maleic anhydride. Castor oil, after heat treatment in presence of catalyst (100 pts.), is heated at 120°–130° C.[41] for four and a half hours approximately with maleic acid (35 pts.) to yield a resin.

Another castor oil compound, described as a resin-plasticiser, is obtained when castor oil and glycerol are heated together in the presence of litharge at 230° C. A further addition of glycerol is made, maleic acid added and the heating continued until the resin is produced.[42]

Castor oil, a monohydric alcohol and a partial ester of maleic acid are heated to form a resin.[43]

A reaction also occurs between maleic anhydride and vegetable oils containing non-conjugated systems,[44] such as linseed, poppyseed, perilla and olive oils. Higher temperatures, that is, temperatures in excess of 180° C. are necessary for the reaction with non-conjugated oils.

Stand oils of improved dry and water resistance capable of very rapid production, are obtained by heating linseed oil at 200° C. with up

to 10 per cent of maleic anhydride, which is believed to act catalytically. The acidity of the resultant oils is reduced by esterification with polyhydric alcohol.[45]

Maleic anhydride-unsaturated vegetable oil compounds may be used as plasticisers for nitrocellulose. The product from wood oil may be used as a constituent of oil-modified alkyds.

Maleic or fumaric acid is first heated with trimethylene glycol, or mono, di or triethylene glycol. This yields a strongly acid resin by condensation with rosin. A mixture of drying oils or their fatty acids and glycerol is added and the heat treatment continued.[46]

A resin is obtained by heating a mixture of maleic anhydride, glycerol, unsaturated fatty acid and cyclohexanol.[47] A product is first formed from a terpene and maleic anhydride. This is then reacted further with a fatty acid and a polyhydric alcohol.[48] The resultant resin is soluble in oil. An oil soluble resin is claimed also by reacting maleic acid with the glycerol diester of vegetable oil acids.[49]

Other Resinous Maleic Anhydride Compounds

There are a number of interesting resinous compounds containing maleic acid or anhydride and these should be included for completeness.

By the action of heat or light on esters of maleic or fumaric acids, assisted by the presence of benzoyl peroxide, clear soluble resins are obtained. These may be stoved for one hour at 65° C. to yield tack-free films.[50] Glycerol may be partly esterified by naphthenic acid, using one molecule of each reactant. The product is then completely esterified by interaction with maleic acid.[51] Rapid hardening resins are obtained by the following three methods. Ethylene glycol and maleic anhydride are reacted together in an atmosphere of carbon dioxide, and benzoyl peroxide is added. Diethylene glycol, maleic anhydride and naphthalene-2-sulphonic acid are reacted together and benzoyl peroxide added, or ethylene glycol, maleic anhydride and phthalic anhydride are reacted and benzoyl peroxide added as before.[52]

Resins are claimed from the interaction of maleic anhydride and rubber in the presence of benzoyl peroxide. Alternatively, maleic anhydride is reacted with rubber and a phenol, and the resultant product condensed with formaldehyde.[53] Divinyl acetylene reacts with maleic anhydride and the product can be esterified with glycerol to yield a resin.[54] Hard resins are obtained from maleic anhydride and vinylhydrindenes.[55]

Resinous compositions are obtained by the co-polymerisation of maleic anhydride with substances of the type of acrylic acid or its esters, styrene, and vinyl esters or ethers.[56]

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Coumarone Resins

Source.—The basic raw material used for the manufacture of these resins is coal-tar naphtha. It is the coumarone and indene constituents of it, capable of polymerisation, which are the resin-forming compounds. Dicyclopentadiene may be polymerised also by heating to yield a resin. Pure coumarone is a liquid of boiling-point 172° C. Pure indene is also a liquid, boiling-point 182° C.

Manufacture

Polymerisation Catalysts.—Coumarone is polymerised to a resin by the action of the following substances: sulphuric acid, stannic chloride, aluminium chloride, phosphorus oxychloride, oxygen,[1] tin tetrachloride,[2] ferric chloride, ferric acid sulphate,[3] boron trifluoride.[4]

Indene is polymerised to a resin by the action of the following substances: sulphuric acid, hydrogen fluoride, boron trichloride, stannic chloride, antimony trichloride, antimony pentachloride, titanium tetrachloride, oxygen,[5, 6] phenyldiazonium fluoroborate, perbenzoic acid,[7] tin tetrachloride,[2] ferric chloride and ferric acid sulphate.[3] Light and heat also aid polymerisation of indene.

Partial polymerisation of indene occurs with hydrochloric, phosphoric and acetic acids. Chlorides of aluminium and zinc are equally effective.[8]

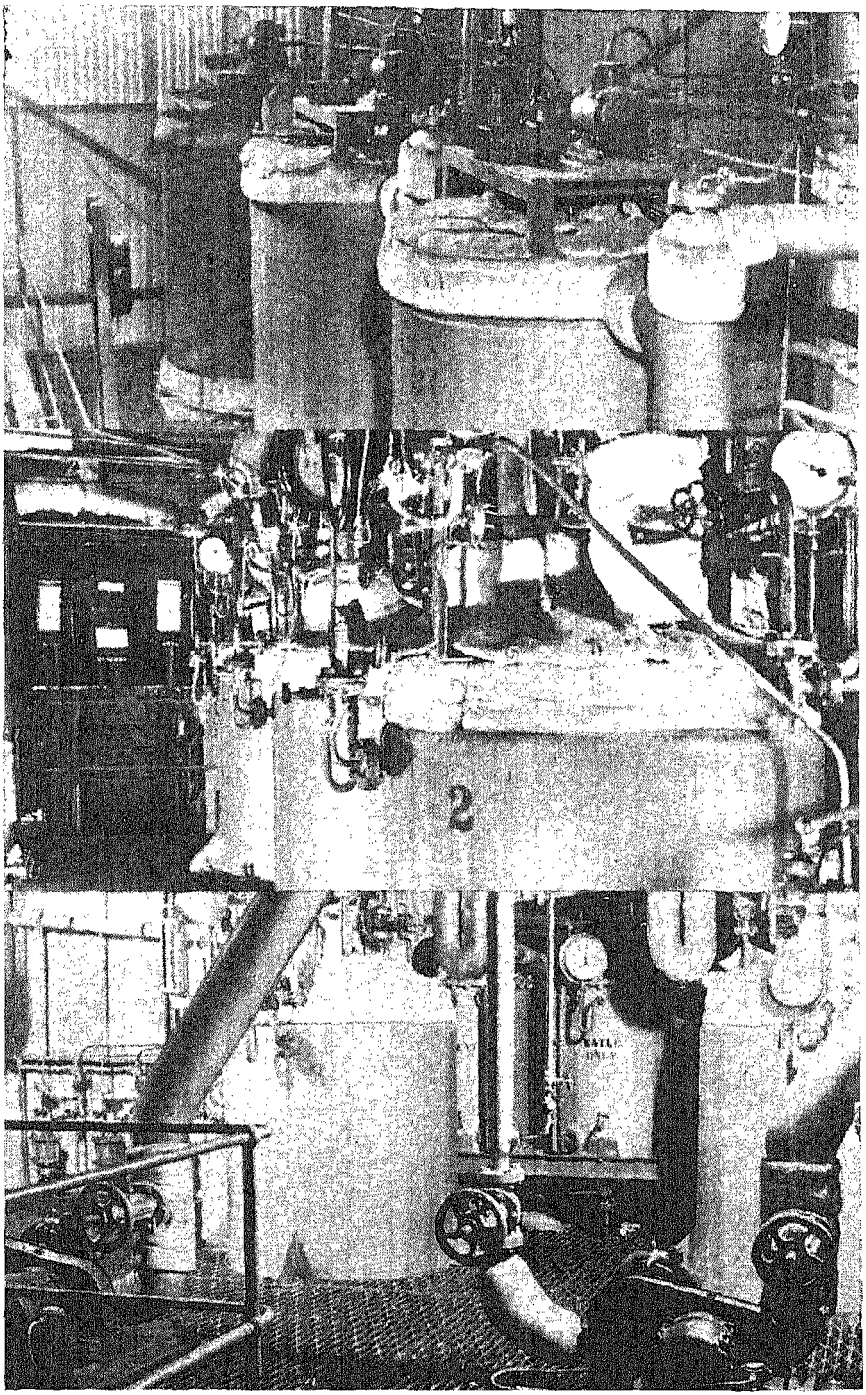
An approximately neutral activated clay is used as a polymerisation catalyst at elevated temperatures for substances in solvent naphtha more reactive than coumarone or indene.[18] Activated clays may be used also for polymerisation of coumarone and indene.

The Form of Acid Catalysts.—When sulphuric acid is used as a polymerisation catalyst it may be used in various forms. It may be diluted with glacial acetic acid, or used as a solution in isopropyl ether. Another catalyst is derived by heating together two molecules of sulphuric acid with one molecule of a saturated aliphatic ether. A mixture of boric and sulphuric acids is sometimes used, and this is stated to be useful in the production of pale resins.[9]

Manufacturing Methods.—To prevent serious overheating due to the exothermic nature of the polymerisation of indene, the reaction is conducted in a solvent and the reaction mixture may be artificially cooled.

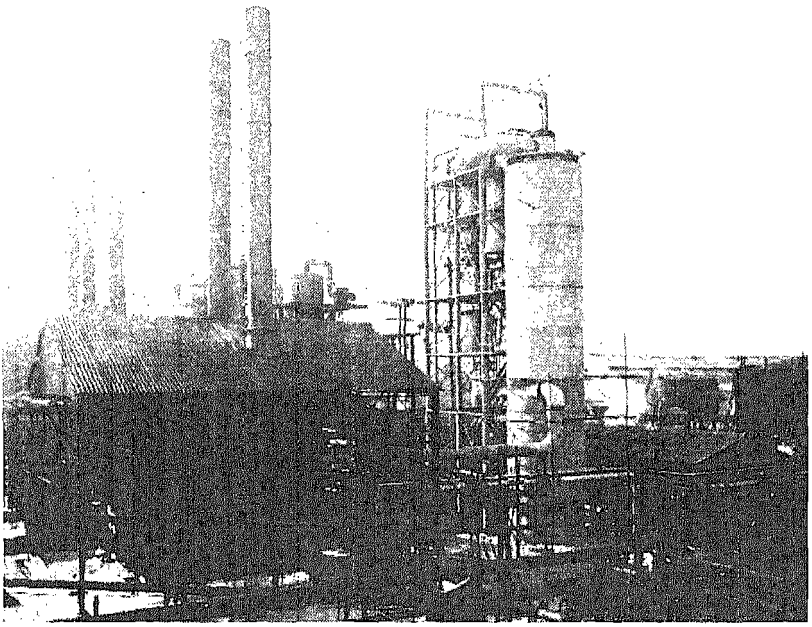
So-called coumarone resins are usually mixtures of polymers of coumarone and indene, for these constituents are rarely separated.

Ellis has divided the manufacture of coumarone resins into seven distinct steps.[10] The first consists in refining the solvent naphtha used. The naphtha is fractionally distilled to yield a fraction boiling-point 160°–180° C. (approx.). Phenols, naphthalene, tar acids, pyridine and quinoline are next removed. The naphtha is then dried by careful acid treatment which is simultaneously instrumental in removing certain undesirable hydrocarbons. Polymerisation of the dry refined naphtha is then effected by the careful addition of catalyst with constant stirring



TYPICAL STYRENE POLYMERISING POTS.

To face p. 208.



VACUUM DISTILLATION PLANT FOR PRODUCTION OF ASPHALTIC BITUMEN FROM PETROL.

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and cooling. Of the catalysts used, sulphuric acid is the most popular. When polymerisation is complete the reaction mixture is allowed to stand to enable the heavy acid sludge to settle. This is removed, and the acidity of the residual oil is neutralised by the addition of caustic soda. The resin solution is separated from the caustic soda solution and washed free of excess alkali with water. The resin solution is finally distilled under vacuum and the resin is left behind as a non-volatile residue. The distillation may be conducted with or without the presence of steam.

The Effect of Process on Resin Properties. Effect of Catalyst, Temperature, Time, and Oxidation.—The properties of the resin may be changed substantially by the manufacturing process. The concentration of the acid catalyst is important. If the concentration is too high dark products are obtained; if it is too low the melting-point of the product is correspondingly low. High polymerisation temperature causes darkening of the resin. Time during which the dark acid sludge is allowed to remain in contact with the resin solution is another factor which influences the colour of the final product. During the final distillation of the resin solution to obtain the resin residue, temperatures should be kept as low as possible in order to avoid discoloration. Duration of the polymerisation process has an important bearing on the properties of the final product. Solubility of resin decreases with increase in acid concentration.

Oxidation is prevented during the polymerisation process using sulphuric acid, by conducting it in the presence of aniline sulphate or pyridine sulphate.[11] Pale resins are obtained.

Refining. Colour.—Impurities which confer colour on resins are absorbed by dissolving the resin in an aliphatic hydrocarbon. A clay is mixed with this solution. A similar result is obtained by heating the resin with a clay capable of absorbing the colouring matter.[12]

Modified Coumarone Resins

Coumarone-indene resins may be hydrogenated. The resin is placed in contact with hydrogen and a catalyst, at a temperature between that of the ordinary atmosphere and that causing decomposition of the resin. Traces of substances which might poison the hydrogenation catalyst are first removed.[13]

Coumarone resins may be dehydrogenated. Sulphur is mixed with the resin and the mixture heated at 180° C. The resins obtained have better solubility in aliphatic hydrocarbons and they are less susceptible to atmospheric oxidation.[14]

Modified coumarone resins are produced for certain purposes. A high grade varnish resin of high melting-point is obtained from a mixture of coumarone resin and pure phenolic resin. Coumarone resin is heated at 200° C. with 20 per cent of a *p*-amyl phenol-formaldehyde condensation product.[15] The presence of phenols during the polymerisation of

coumarone and indene is stated to confer alcohol solubility on the resultant resin.[16]

Coumarone-styrene resins are other recent and interesting products. They are not, however, so soluble as the coumarone indene resins. They dissolve in aromatic hydrocarbons, esters, and terpenes to give very viscous solutions. They are insoluble in drying oils.

Properties

Colour. Form.—Coumarone resins are brittle products, varying in colour from a pale straw to a reddish-brown. Some varieties are almost black. The most popular form is as small thin flakes and these aid solubility.

Solubility. Compatibility.—Most coumarone resins commercially available are readily soluble in petroleum hydrocarbons such as white spirit, to give a clear or faintly opalescent solution. Other grades are only partly soluble in white spirit and need the addition of stronger solvents. Coumarone resins are soluble in aromatic hydrocarbons, chlorinated hydrocarbons, turpentine, most esters, carbon disulphide and ethers of ethylene glycol. Normally coumarone resins are insoluble in alcohols, although special grades are soluble. Mixed solvents have been suggested for coumarone resins, and a blend of 91 parts benzine with 9 parts acetone, or 92 parts benzine with 8 parts of butyl glycol β-ethyl ether, are two examples.[17] Vegetable oils are quite miscible with coumarone resins, and this makes them valuable for certain types of varnish. It is often necessary to use heat to effect solution of coumarone in heavy stand oils, and for heavy blown oils a preliminary treatment with a thin stand oil is recommended. Coumarone resin is miscible with most of the common varnish constituents, including petroleum and coal-tar pitches, natural asphaltums, ester gum, rosin, limed rosin, phenolic resins, natural copals and chlorinated rubber.

Plasticisers.—Coumarone can be plasticised if necessary, and among the most satisfactory plasticisers may be included tricresyl phosphate, ethyl abietate, vegetable oils (including castor oil), triphenyl phosphate, diamyl and dibutyl phthalates and butyl stearate. It should be noted, however, that the solubility of this resin may be influenced appreciably by its degree of polymerisation.

Melting-Point.—The melting-point of coumarone resins varies considerably, from less than 40° C. for the soft grades to above 155° C. for the hardest grades. For varnish manufacture resins with melting-points around 130°–140° C. are generally the most satisfactory. Liquid coumarone resins may be used also for special purposes such as plasticisers or as adhesives.

Chemical Resistance and Yellowing.—Coumarone is almost neutral, is practically unsaponifiable and is resistant to alkalies and most acids. It tends to darken both on exposure and on heating. The causes of yellowing of coumarone resins were not, until recently, definitely

established. The yellowing of coumarone-indene resins has been explained by Carmody. On the basis that indene is a cyclopentadiene derivative, it reacts with ketones, aldehydes, or oxidised compounds, forming highly coloured bodies known as fulvenes. Indene or polymerised indene is attacked at the double bond by atmospheric oxygen, producing aldehydes or ketones ultimately. These react with unoxidised indene polymers, eliminating water and yielding fulvene compounds.[30]

Smell.—Coumarone can be detected even in oleo-resinous compositions by its characteristic smell, especially if the product is gently heated. The prominence of the odour of coumarone resins varies considerably. Some resins betray only the slightest smell whilst others possess smells which are definitely objectionable. The smell of a coumarone resin is important when it is used in finishes for the interior of buildings.

Detection.—Another method of detecting this resin is by means of the Liebermann-Storch reaction. It gives a characteristic pale pink colour which is unlike the colour given by any other resin. A colour is produced also when 1 c.c. of a 10 per cent solution of resin in chloroform is diluted substantially with more chloroform, and 1 c.c. of glacial acetic acid added. After shaking, 1 c.c. of a 10 per cent solution of bromine in chloroform is added with more shaking, when, on standing, a red colour develops.[16]

Varnish Making with Coumarone Resin

Polymerisation of wood oil is retarded by the presence of coumarone resin. In this respect it is claimed by Kenny to be as effective as limed rosin.[19] In the manufacture of varnishes from coumarone two factors must be kept in mind. Firstly, that to effect clear and stable solutions with the various types of varnish oils some cooking at temperatures of approximately 230°–260° C. is necessary. The second factor is that cooking in excess of 280° C. causes darkening of the resin. Ellis states that the darkening may be due either to thermal decomposition or to the presence of sulphonated compounds.[20] For this reason the temperatures used for the distillation process in the final stages of production of the resin are kept to a minimum.

To produce varnishes or lacquers from coumarone resin the following methods have been recorded. A straight solution of the resin in white spirit, or white spirit-naphtha mixtures, can be obtained by melting the resin, removing from the source of heat and adding the solvent slowly with constant stirring. A slower process is to dissolve the resin by cold churning. From the latter method the solutions produced are paler. For short wood oil varnishes it is suggested [18] that the bulk of the resin is dissolved in wood oil at 205° C. and the temperature of the mix raised to 290° C. It is checked immediately with the remainder of the resin and bodied to the desired viscosity at 230° C. For long wood oil varnishes a somewhat similar process is adopted except that the wood oil is heated to a high temperature rapidly and then checked with rosin. Coumarone is

added and the bodying conducted at 230° C. as before. King [21] heats wood oil to 245° C., adds the coumarone resin and bodies at 280° C. If the varnish includes pure oil-reactive phenolic and coumarone resin, both resins may be added to the wood oil at 205° C., and the mixture held for ten minutes. The temperature may then be raised to 240° C. until the desired body is attained when the whole is rapidly chilled. This is the best procedure to adopt when the ratio of oil to resin is less than 2½ oil to 1 of resin. For longer oil mixtures containing this combination of resins the bodying temperature can be raised to 260° C.

Coumarone varnishes have a tendency to bloom when made at temperatures below 295° C,[22] but if high temperatures are used to eliminate this tendency then, as mentioned already, darkening must be expected. Greenfield [23] confirms that insufficient cooking causes blooming.

It has been stated that the low acidity of coumarone resins prevents the use of driers such as litharge and manganese dioxide. It should be emphasised, however, that when drying oils are present these are saponifiable, and are capable of absorbing driers irrespective of the nature of any resin which may be present, provided that the driers are incorporated by high temperature treatment. It is probably true, however, that lead driers thus incorporated may precipitate out on standing more readily from varnishes containing coumarone resin than from varnishes containing acidic resins. Lead resinate is recommended as the best soluble form of lead drier for use with coumarone resins to minimise the tendency to subsequent precipitation.[24] Cobalt resinate is claimed to give better results as a drier than the linoleate.[23]

Uses

The neutrality of coumarone resins makes them valuable components of metallic lacquers, insulating varnishes and non-feeding gold-sizes. In metallic lacquers low acidity prevents gelation on storage due to interaction of free acid in the medium with the metallic powder. It minimises loss of metallic lustre due to prolonged storage or on ageing of the film, and prevents the evolution of gases which may, in bad cases, burst the containers. Flotation of metallic flakes also seems to be better in films of low acidity although this property is influenced also by viscosity of the film and properties of the thinners present.

In insulating varnishes coumarone resin is a popular choice because its low acidity prevents corrosion of copper wire which might occur during stoving or on ageing. Furthermore, it has a satisfactory dielectric strength. Electrical resistivity is claimed to be higher than that for shellac. It is used to increase the viscosity of hydrocarbon oils for impregnation of insulating paper for cables.[25] With insulating varnishes some specifications stipulate that the acidity of the dried varnish film should be within certain limits. The use of coumarone resin aids in the accomplishment of this objective. Coumarone is a suitable resin whether used in the short oil type of insulating varnish for impregnation of coils

or in the long oil type used for the manufacture of insulating tape. Varnishes for coil impregnation will be based on wood oil with coumarone alone or in admixture with ester gum, limed rosin or pure and modified phenol formaldehyde resins.

The coumarone resins used for this purpose should be of a type easily soluble in petroleum hydrocarbons, for the presence of aromatic hydrocarbons would cause the enamel on copper wire to be softened or removed. Varnishes for impregnation of fabric for the production of insulating tape will be based on linseed stand oil chiefly, with the possible addition of wood oil. The resins will be as used for the shorter type of impregnating varnish recorded above.

The neutrality of coumarone resins is exploited in non-feeding gold-sizes. A very cheap gold-size based on a simple solution of limed rosin in white spirit with the possible addition of a little stand oil sometimes feeds with zinc oxide or white lead. This tendency can be reduced considerably by the substitution of part of the limed rosin by coumarone resin.

Coumarone resins are chemically inert and they are resistant to most acids, alkalies and salts. Lactic and acetic acids have no effect on them.[26]

Apart from the fact that coumarone resins are chemically inert they are resistant to most acids, alkalies and salts. Lactic and acetic acids have no effect on them.[26]

Their alkali resistance makes coumarone resins popular constituents of varnishes or sealing solutions for cement or plaster. Excellent protection can be obtained by wood oil-coumarone resin, wood oil-coumarone resin-phenolic resin, or chlorinated rubber-coumarone resin combinations. Bituminous compositions for acid resistance may be hardened by the addition of coumarone resins.

Other uses for coumarone resins include their incorporation in: gloss oils, media for toy enamels, spar varnishes, floor varnishes, nitrocellulose lacquers, rust preventing solutions for iron and steelwork, media for anti-fouling paints, gold stoving varnishes for tinplate, waterproofing compositions for fabric, paper, leather, etc., adhesives, in solutions for coating electrodes of electroplating cells to prevent deposition of metal,[27] in black japans and black lacquers, in printing inks, in alcohol resisting finishes, in binding compositions for floors and roads, for addition to rubber to produce hardness and gloss, in injection moulding [28] and in the manufacture of linoleum.

When coumarone is used in nitrocellulose lacquers the presence of other resins is necessary to provide compatibility since coumarone and nitrocellulose are not compatible alone. Ester gum has been suggested as a suitable resin for this purpose.[29]

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Urea Formaldehyde Resins

The value of urea formaldehyde resins may be attributed chiefly to their ready compatibility with alkyds to yield excellent stoving finishes.

Chemical Constitution.—Formaldehyde reacts with amides to yield resins. Urea is a typical amide. The chemical constitution of the final reaction product has been the subject of much experimental and theoretical consideration, but it is still controversial. Among workers on the subject must be included Goldschmidt, Dixon, Hodgins and Hovey, de Chesne, Hölzer, Walter, Hug, Kadowaki, Lüdy, Einhorn and Hamburger, Van Laer, Scheibler, Trostler and Scholz, Walter and Oesterrich, Walter and Gewing, Bardarelli, and Redfarn.[1]

Amides.—Amides other than urea, which are recorded as having formed compounds with aldehydes, are thiourea, toluenesulphonamide, naphthalene monosulphonamide, ethylideneurea.[2]

Aldehydes.—Aldehydes other than formaldehyde, which have yielded resinous substances with amides, include trioxymethylene (paraformaldehyde), acetaldehyde, furfural, acrolein, benzaldehyde and aldol.

Urea and formaldehyde are condensed together in aqueous solution. Alternatively, the reaction may be conducted in a solvent, when the resultant resin has better solubility.[3]

Condensing Agents

A 40 per cent solution of formaldehyde and urea are heated to yield a resin.[4] The reaction may be facilitated by the addition of small amounts of acidic or alkaline condensing agents.

Acid Condensing Agents.—Acid condensing agents are sulphuric, hydrochloric, nitric, phosphoric, acetic, oxalic and tartaric acids,[5] as well as acid salts.

Alkaline Condensing Agents.—Alkaline condensing agents are sodium acetate, borax, ammonia, hexamethylenetetramine and pyridine.[6]

Other Condensing Agents.—Other condensing agents include carbonates of lead, zinc, calcium and magnesium, titanium oxide, hydrogen peroxide,[7] the citrate, tartrate and lactate of titanium, aluminium salts for aiding in the production of the primary condensation product, low melting-point monohydric phenolic compounds, and sulphonated amides. Powdered zinc is stated to retard catalysis.[8]

Reaction between Urea and Formaldehyde

In Absence of Solvents.—Zinc chloride (57 pts.) is added to 37 per cent aqueous solution of formaldehyde (275 pts.) after which urea (100 pts.) is stirred in. Condensation at ordinary pressure is effected in a few seconds by adding aqueous formaldehyde solution to fused urea in the presence of an acid catalyst.[9] The solid polymer of formaldehyde is mixed with urea or thiourea and maintained at 15°–35° C. until the smell of formaldehyde disappears.[1]

The importance of the hydrogen ion concentration during condensation has been emphasised by Redfarn.[1] He suggests that 4·5 is a satisfactory figure and that this is attained by means of formic acid which may be derived from formaldehyde.

Urea and formaldehyde are blended with an acidic solution of hydrogen ion concentration of 4–7, and these limits are maintained during condensation by heat, by the addition of an inert buffer. Urea (1 mol.) is added gradually to a 40 per cent aqueous formaldehyde solution (2 mols.), addition of dilute acid of hydrogen ion concentration 1·5 causes precipitation of the resin which is removed, washed and dried. A sulphite condensing agent is used for the initial condensation stage of urea and formaldehyde, and a small quantity of acid is added for the completion of condensation. It is suggested also that softening agents may be incorporated during condensation.

In Presence of Solvents.—Condensation is effected in the presence of solvents such as alcohol. Urea and formaldehyde are condensed in the presence of butyl alcohol. A resin soluble in butyl alcohol, permitting the addition of substantial amounts of aliphatic and aromatic hydrocarbons is obtained.[11] Reference is made elsewhere to the use of solvents for the reaction containing at least one hydroxyl group, and of high molecular weight saturated or unsaturated alcohols.[12]

Varnish Constituents

A resin soluble in hydrocarbons is obtained by reacting urea or thiourea and formaldehyde in alcohols. Acetaldehyde or benzaldehyde may partly replace formaldehyde. Alcohols such as ethyl, butyl and propyl alcohols are used at their boiling-points, but higher boiling alcohols such as mono-ether of ethylene and diethylene glycol and cyclohexanol are maintained below 120° C. The use of octyl alcohol has become popular. Water should be absent but volatile acidic catalysts like formic, acetic and hydrochloric acid are used. Water eliminated by the reaction is distilled off as produced.[13]

Amounts equivalent to one molecule of urea and two molecules of aqueous formaldehyde in butyl alcohol are heated to the methylol stage. Formic acid (0·06 per cent) is added and the whole refluxed under reduced pressure below 80° C. for thirty to sixty minutes. Any butyl alcohol distilling off with the water is replaced as it is lost. Distillation is carried out finally at ordinary pressure, until a quantity of water equivalent to two molecules has been collected.[14] Condensation of urea and formaldehyde may be effected satisfactorily in the presence of primary, secondary, tertiary or polyhydric alcohols. After the reaction the product is neutralised with the lactate, chloride, carbonate or acetate of ammonium, an amide or a derivative thereof. The function of these agents is to remove free formic acid. A solution of acetanilide in water is stated to confer fluidity upon the reactants to permit easy dehydration.[15] In another process urea, formaldehyde and ammonium lactate, chloride, acetate or carbonate, or an amide or derivative thereof, are reacted together. After the reaction, methyl alcohol and then silica, zinc or aluminium oxide are added. The solution, after boiling, is filtered to remove insoluble matter, aqueous acetanilide is added and the whole dehydrated.[16] In order to conduct the reaction under anhydrous conditions, anhydrous butyl alcohol is used with calcium chloride.[17] Acid condensation of the methylol compound of urea is conducted in ethyl or butyl alcohol with higher alcohols such as those obtained from the acids of palm kernel oil. The product is neutralised with trisodium phosphate, and after solvent is distilled off, the residue is heated at 80°–130° C. until a hydrocarbon soluble resin is obtained.[18]

The use of anhydrous conditions is emphasised in a patented process,[19] which specifies the use of anhydrous reactants and an anhydrous reaction solvent.

Resin Formation

Alkaline Condensing Agents.—Although most of the published work is concerned with the use of acid condensing agents, alkaline condensing agents, as indicated already, may be used also. A mixed reaction solvent of water and organic ester is used to condense urea or thiourea with formaldehyde, in the presence of alkaline compounds. Organic solvents are formates or acetates.[20]

1·5 to 2·5 mols. of formaldehyde are condensed with one molecule

of urea or thiourea in the presence of small amounts of methylamine, ethylenediamine, or a phenylenediamine and a weak acid. Other nitrogen compounds which may be used for condensation of urea with formaldehyde include amylamine, aniline, and hydroxylamine, and the reaction is stopped by the addition of compound which neutralises the nitrogen compound with the formation of an inactive addition compound.[21]

Activated charcoal is used to absorb acidic bodies produced during condensation or it may be added to the reactants before the reaction is started. In the former instance resins of exceptional paleness are obtained. When charcoal is added before the reaction is conducted a description of the method is as follows: urea (600 pts.) is dissolved in 37 per cent formaldehyde (1620 pts.). To this solution activated charcoal (80 pts.) is added. After filtration the mixture is held at 100° C. for eight hours.[22]

Methylolureas.—Resins may be prepared also by first forming methylolureas. These are merely condensation products of urea and formaldehyde. Dimethylolurea, melting-point about 126° C., can be made by reacting together urea and formaldehyde in the presence of barium hydroxide.[23] Resins are obtained from methylolureas by continued heating or by the addition of basic or acidic compounds. Dimethylolurea can be prepared also under acid conditions. Subsequent heat treatment at 125°–150° C. yields a resin.[24]

Another method of treatment of dimethylolurea consists in adding urea to a boiling aqueous solution of it. Water is removed by vacuum distillation and the product is polymerised further by acid treatment. The function of the urea is to react with any formaldehyde eliminated during subsequent condensation.[25]

Ethylidene urea.—Ethylideneurea, made by reacting urea and acetaldehyde together in the presence of an acid for several days at ordinary temperature, is reacted further at 70° C. with formaldehyde to yield a resin.[26]

Modified Urea Formaldehyde Resins

Many modifications of the simple urea formaldehyde condensation product have been attempted, but the most interesting and useful from the varnish maker's point of view are those which possess improved compatibility and solvent properties. Urea base resins are now available which are soluble in or which permit considerable dilution with both aliphatic and aromatic hydrocarbons. In addition they are miscible with ordinary and bodied vegetable drying oils.

This improvement in solubility is affected by the introduction of suitable aliphatic alcohols into the urea-formaldehyde product. Alcohols which are used for this purpose include butyl, amyl, octyl and capryl alcohols.

The following patented process gives some idea of the type of procedure involved. Formaldehyde and urea are condensed together at 60°–90° C. in the molecular ratio of 2·5 : 1 under alkaline conditions, until

80 per cent of the formaldehyde has reacted. After removal of water under vacuum, the product is etherified by heating with an excess of monohydric alcohol under slightly acid conditions, until homogeneity is attained.[51]

The other method of improving general compatibility is by the introduction of melamine into the urea and formaldehyde reactants, and composite resins of this type are marketed. Urea formaldehyde resins soluble in vegetable oils are made by fusing the reaction product of urea and formaldehyde with fatty acids, vegetable oils, hydrocarbons, or high boiling esters.[29] A urea formaldehyde product made in an alcoholic solvent is heated with an ester derived from fatty acids and polyhydric alcohols, containing a minimum of one free hydroxyl group. The reaction is conducted in a solvent which is not miscible with water and continued until the resultant product is soluble in aromatic hydrocarbons.[37]

A low temperature stoving medium is derived from an oil modified urea formaldehyde resin made by the interaction in alcohol of urea, formaldehyde and a vegetable oil fatty acid at 100° C.[30] Furfural, urea and wood oil have been condensed together.[27] Urea and phthalic anhydride are first reacted together and the product reacted further with an aldehyde to form a resin.[28]

A product for making textiles resistant to corrosive attack, is derived from a compound made by condensing urea and cresylic acid with formaldehyde in the presence of zinc acetate. After dehydration this is blended with an alkyd resin.[31] Thiourea, urea, glycol monoacetate and formalin are reacted together in the presence of caustic soda to yield a resin.[32] The product of phthalic anhydride (4 mols.) and glycerol (3 mols.) is refluxed with urea and formaldehyde in butyl alcohol. A resinous coating composition is obtained.[33]

One to 5 per cent of an organic peroxide is heated with an oil modified alkyd. The product is combined with a condensation product of urea and formaldehyde.[34]

In the production of alkyd-urea formaldehyde polymers an excess of polyhydric alcohol may be used, e.g. an unmodified or oil modified alkyd containing an excess of polyhydric alcohol is reacted with the urea formaldehyde product. The resin derived from unmodified alkyd [35] is stated to be miscible with oil modified alkyds and is soluble in hydrocarbons.[36]

Urea (1 mol.), formaldehyde (1 to 2 mols.) and hexamethylenetetramine (0·1 to 1 mol.) are reacted together. Urea may be partly substituted by aniline, phenol, thiourea, acetamide, or oxamide. Other modifying agents which may be added include glycerol, starch, gums arabic and tragacanth, and glue.[38] Intercondensation of urea formaldehyde resins has been conducted with phenols, and long chain unsaturated alcohols, and sulphonamides.[39] Urea resins may be modified by the addition of polymerised β-hydroxytrimethylene sulphide.[40]

The condensation product of a carbonic ester with formaldehyde is reacted in an alcohol under acid conditions, with the condensation product of urea and formaldehyde produced in the presence of an alkali.[41]

Properties and Uses

Condition.—Urea formaldehyde resins are practically colourless. They may be obtained in the form of plastic masses or brittle lumps. It is common also to use viscous solutions of these resins.

Solubility.—They are soluble in alcohols, cyclohexanone, ethers of methyl, ethyl or butyl glycol, and diacetone alcohol ; [42] some types are soluble in aromatic hydrocarbons. Solutions in butyl alcohol tolerate dilution with aliphatic or aromatic hydrocarbons.

Effect of Heat.—The resins provide hard films on stoving, and as indicated already they are especially suitable for use with alkyds, with which they are miscible and on which they confer hardness. Furthermore, they reduce the stoving time of alkyds substantially.

The hardness of urea formaldehyde resins or of compositions containing them is exploited in protective films for surfaces subjected to abrasion, rubbing or rough handling. On stoving urea resins, formaldehyde is evolved and good ventilation is essential. Temperatures over the range 180°–240° F. are the most satisfactory. The resins are resistant to the action of light, in that they show no yellowing tendency. They withstand high temperatures without showing signs of serious decomposition, and Hodgins and Hovey make a point of heat stability at 400° F. Sanderson also confirms colour retention at high temperatures.[43]

Plasticisers.—A film of pure resin obtained by stoving is not of much value in itself as it has a tendency to brittleness and has rather poor adhesion. This may be remedied by the addition of plasticisers, including castor oil, blown castor oil, tricresyl phosphate, esters of phthalic acid, among which is included methyl cyclohexyl phthalate, esters of sebacic acid and alkyds.[44] Alkyds are recommended as plasticisers because they show no tendency to sweat out.

Chemical Resistance.—Stoved films are chemically resistant and resistant to the action of solvents. Resistance to solvents and chemicals is increased by the addition of hydroxynaphthoic, gallic and salicylic acids to solutions.[45]

Acidity.—The low acidity of urea formaldehyde resins makes them useful in the production of stoving metallic lacquers.

Stability of Solution.—When mixed with alkyd resins the solutions are not always stable, and careful selection of solvents is necessary if excessive stoutening or separation is to be avoided. Hodgins, Hovey and Ryan, however, state that admixture with alkyds improves the keeping qualities of urea formaldehyde solutions.[46]

The addition of semicarbazide or carbo-hydrazide to urea formaldehyde resins induces stability against precipitation.[47]

Analysis.—Solutions of urea resin in butyl alcohol can be analysed

by decomposing the resin, subjecting the alcohol or aldehyde to oxidation and titrating the fatty acids obtained. Nitrogen determinations using the Kjeldahl method provide the basis for urea content calculations.[48]

Hardening Agents.—Urea formaldehyde films can be hardened at ordinary temperatures by the addition of acidic compounds. The following acids which may also act as plasticisers have been used for this purpose: lactic, pyroracemic, hydroxypyroracemic and glyceric acids. Other acids which promote hardening include hydrochloric, sulphuric, phosphoric, hydrofluoric, and formic acids. Sulphuretted hydrogen, sulphur dioxide and disodium phosphate have been used also.[49] The effect of acidic substances on the rate of hardening is further illustrated in the claim that acidic pigments decrease the stoving time of urea formaldehyde films. Alkaline pigments have the reverse effect.[46]

Other compounds which act as catalysts are β-naphthyl thiolbenzoate, and thiol or dithiol phthalate.[52]

Other Properties.—Urea formaldehyde resins have greater transparency to light than the corresponding products from thiourea or methylurea.[50]

A defect of urea formaldehyde films is their inferior water resistance particularly on immersion.

Uses.—Urea formaldehyde resins are used in moulding compositions, in stoving metallic lacquers with alkyds, in non-yellowing media for refrigerator finishes, in glass substitutes transparent to ultra-violet light, in safety glass manufacture, in adhesives, in clear lacquers for metals, in nitrocellulose lacquers, in impregnating solutions for textiles and paper, in hat stiffeners, and in cold hardening or low temperature stoving finishes for wood.

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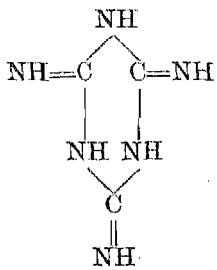
Melamine Resins

The basis of these resins is melamine, which is known also as 1 . 3 . 5 . triamino 2 . 4 . 6-triazine.

Its formula can be represented as



although it exists in three tautomeric forms.

Melamine is a highly reactive substance, containing three amino groups. From the condensation with aldehydes resins are obtained. Reactive modifying agents are included also if desired.

Properties

Compatibility.—Melamine resins show improved compatibility generally by comparison with the urea formaldehyde types. Beetle resin 52 is a typical melamine resin, and like many similar resins it is available as a solution in butanol. This may be diluted extensively with ethyl and butyl alcohols, ethyl, butyl and amyl acetates, acetone, glycol ethyl ether, aromatic hydrocarbons and turpentine. Substantial amounts of white spirit may be added also before precipitation occurs.

Alkyds have been specially developed as plasticisers, and excellent compatibility is shown by alkyds modified with both drying and non-drying oils. Compatibility with the usual range of plasticisers is good, and better than with urea formaldehyde resins. Melamine resins have been suggested for admixture with natural copal-linseed oil varnishes, vegetable oils and urea formaldehyde resins.

Compatibility with cellulose nitrate is excellent.

Thermosetting Properties.—Melamine resins are thermosetting, and temperatures as low as 180°–220° F. are effective, the duration of heating varying from half to one hour. At 250° F., ten to twenty minutes' heating suffices. These stoving conditions are an improvement on those used for urea formaldehyde resins, which require half to one hour's heating at 250° F.

The hardening of melamine resins on heating has been studied by Kohler, who followed the process by estimating the reduction in solubility in pyridine.[3]

Heat Stability.—Another outstanding feature of these resins is their resistance to degradation on heating. Maintenance of colour, gloss, and adhesion, at 400° F., is possible with combinations of melamine resin and alkyd plasticiser.

The comparative heat instability of urea formaldehyde resins has been attributed to the presence of the carbonyl group, which is, of course, absent in melamine resins.[1] Melamine resins also possess good light resistance.

Chemical Resistance.—Melamine resin finishes show superior resistance than urea formaldehyde resins to water, acids, alkalies and solvents.

Durability.—There is not much published work on the durability of melamine resins, but there are indications that it is superior to urea formaldehyde resin for resistance to chalking in pigmented enamels. Sanderson reports that certain air-drying alkyds, especially when used with oxidation inhibiting pigments, show improved weather resistance after additions of melamine resin.[2]

Electrical Properties.—Heat-hardened melamine resin is a good electrical insulator and has excellent non-tracking properties.

Uses

The chief use of melamine resins is in the production of non-yellowing stoving enamel media, in conjunction with alkyds, their property of

rapid hardening at low temperatures being valuable in reducing heating costs and increasing output. These types of enamel are used on refrigerators.

Resistance to petrol, grease and lubricating oil promotes their use in finishes for motor-cars.

Heat resistance is exploited in finishes for radiators, heaters, irons, etc.

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Polystyrene Resins

Polymerisation Mechanism.—Polystyrene resins, as their name implies, are simple polymerisation products of styrene. The mechanism of the polymerisation process and the molecular structure of the polymers obtained have been studied by a small army of workers among whom may be included: Staudinger, Dostal and Mark, Risi and Gauvin, Roff, Staudinger and Steinhofer, Mizushima, Morino and Inoue, Midgley, Henne and Leicester. de Boer, Houwink and Custers, Signer and Weiler, Whitby, Flory, Signer and Gross, Shulz, Shulz and Husemann, Bergmann, Suess, Pilch and Rudorfer, Norrish and Brookmann, and Prettre.[1]

Factors Influencing Speed of Polymerisation.—Polymerisation of styrene may be effected on styrene alone or in a solvent. It may be aided by the presence of heat, light, electromagnetic fields,[2] and catalysts. Catalysts may be oxidising, acidic or alkaline compounds.

The rate of polymerisation of styrene to form a resin increases with increase of temperature. At 100° C. polymerisation of styrene requires three days; at 200° C. the requisite time is only thirty minutes.[3]

The Effect of Temperature of Formation on Resin Properties.—The resins obtained at low temperatures are claimed to have higher molecular weights than those from high temperature treatment.[4] Stanley records that the mean molecular weight of styrene polymers is constant for any given temperature of polymerisation and is independent of the extent of the polymerisation reaction.[5] Properties of styrene polymers vary with temperature of formation. The resin formed at low temperatures is tough in contrast to the brittle resin resulting from high temperature treatment. Differences in solubility also occur. The high temperature polymer is soluble in ether but the low temperature product is insoluble.[6] The more highly polymerised the resin the greater the viscosity of the resultant solution. A slow polymerisation at low temperature yields resins with good electrical and mechanical properties. When polymerisation is conducted at 85°–90° C. resins of improved rigidity are obtained. The resins are also claimed to have good heat resistance and

good electrical properties.[4] Since temperature of polymerisation influences the degree of polymerisation and this in turn controls the compatibility of the resultant resin, then it follows that temperature of resin formation controls compatibility. Stanley states that polystyrene of molecular weight 2000–3000 can be incorporated with drying oils. Jordan confirms that certain types of styrene resins can be dissolved in linseed oil.[7] Increasing the molecular weight of styrene polymers improves the mechanical properties.

Among other characteristics of polystyrene resins which vary with molecular weight of polymer are appearance, melting-point and solubility. Low molecular weight polymers are liquids, and as the molecular weight increases the resin changes to a white powder and finally to a fibrous condition. The melting-point gradually increases with degree of polymerisation whilst solubility in ether decreases.[8]

Polymers with molecular weights of the order of half a million are now produced, but all such claims of high molecular weight products must be received with caution, because of the difficulties of accurate measurement.

Another interesting fact concerning the influence of temperature on the properties of the resin obtained is that by maintaining a styrene polymer at a temperature (80°–130° C.), substantially below its depolymerisation temperature for a long time, it is possible to raise its softening point above 66° C. The final product is said to be heat resistant.[9]

Polymerisation of gaseous styrene has been effected by heating at a temperature of 249° C. Products possessing a molecular weight up to six times that of the original styrene have been obtained.[10]

Maintenance of polystyrene at temperatures in excess of 300° C. causes depolymerisation.[11]

Catalysts.—The rate of polymerisation of styrene is increased by subjecting it to the influence of ordinary light, or ultra-violet light.[12] The presence of activated oxygen or benzophenone and benzanthrone [13] assists polymerisation conducted under the influence of light.

Catalysts which have been used to promote polymerisation of styrene are oxidising substances including oxygen, perbenzoic acid, benzoyl peroxide, benzoyl hydrogen peroxide, hydrogen peroxide, peroxides of triphenyl methyl, asymmetrical diphenylethylene, phellandrene, and cyclohexene.[14] The presence of peroxides in liquid styrene has been given as the reason for the difference in polymerisation rates of liquid and gaseous styrene.[15] When polymerisation of styrene is effected in the presence of oxygen, oxidation of the product may occur simultaneously. Such oxidation may be catalysed by anthracene, perbenzoic acid, iodine, and compounds of cobalt.[16]

Acids and acidic substances may be used as polymerisation catalysts for styrene. The following acids have been used: hydrochloric, hydrofluoric, sulphuric, chromic, sulphur dioxide, and borofluoracetic acid.[17] According to Williams, hydrochloric acid, under certain conditions, may

act as an inhibitor of polymerisation temporarily. It acts as an inhibitor when styrene in carbon tetrachloride is being polymerised with tin tetrachloride as catalyst. A polymerisation reaction which is inhibited initially may be due to the use of an impure catalyst, the impurity being hydrochloric acid.[18] Other acidic catalysts for styrene polymerisation include aluminium chloride, stannic chloride, boron trifluoride, zinc chloride and titanium tetrachloride.[19]

Alkaline catalysts for styrene polymerisation include not only sodium itself but compounds of sodium and other alkali metals such as hydroxides, etc. Organic bases may be used also.[20]

Effect of Solvent on Resin Formation.—Polymerisation of styrene can be effected in solution. Increase of dilution with solvent reduces the rate of polymerisation.[21]

The influence of concentration in toluene on polymerisation has been studied by Dostal and Jorde. The effect of the walls of the reaction vessel was studied simultaneously.[22]

If the solvent chosen is a solvent both for styrene and polystyrene, a solution of resin is ultimately obtained. Alternatively, if a non-solvent for the resin is used it is obvious that the resin will separate as formed. Among solvents used for styrene polymerisation are : toluene, ethane, propane or butane, carbon tetrachloride, tetrachlorethane, dichlorethane, ethyl benzene, diethyl benzene, heptane and benzene, xylene, dioxane, and decahydronaphthalene.[23] Catalysts may be used to stimulate polymerisation in solution.

The velocity of polymerisation in toluene is twice that in carbon tetrachloride. Mark and Raff have studied the rate of polymerisation of styrene in toluene solutions at various temperatures in the range 60°–98·2° C. At low temperatures a pronounced induction period is reported.[24] Styrene, solvent and catalyst, are mixed together and introduced into a reaction vessel below − 40° C. As this mixture is introduced, the mixture of polystyrene and solvent is removed simultaneously.[25] Brietenbach, Springer and Abrahamczik have shown when the polymerisation of styrene is conducted in carbon tetrachloride that the reaction products contain, not only polystyrene, but a volatile liquid (boiling-point 135° C./0·01 mm.). The composition of this liquid corresponds with an equimolecular mixture of carbon tetrachloride and polystyrene. The polymerisation process was conducted at 140° C. for five to sixty-three hours.[26]

Polymerisation Inhibiting Agents.—Certain substances act as inhibiting agents for the polymerisation of styrene. They are sometimes added to the reaction mixture to arrest polymerisation. Inhibiting agents which have been recorded include hydrochloric acid under certain conditions,[18] hydroquinone, quinone,[23] sulphur, cresol and pyrogallol, trinitrobenzene,[27] and anthracene.[14] The polymerisation of styrene at 100° C. in toluene is arrested, temporarily, by addition of hydroquinone. The presence of quinone causes the formation of low polymers.[23] Goldfinger, Skeist

and Mark have studied the inhibiting effect of benzoquinone on the thermal polymerisation. The length of the induction period was found to be proportional to the concentration of the inhibitor, and after this period the rate of polymerisation was inversely proportional to the concentration.[55] The effect of sulphur on styrene polymers has been examined by Jenckel and Uberreiter.[28]

Determination of Progress of Reaction.—The extent to which polymerisation of styrene has progressed can be determined by distilling off unchanged monomer. On the basis that bromine adds on to polystyrene only in negligible amount, Williams traces the extent of polymerisation, by adding an excess of bromine to the reaction mixture and back titrating. Williams has shown also that the amount of styrene polymerised, as determined by bromination, compares with the polystyrene precipitated by methyl alcohol.[29]

Modifying Styrene Resins

Many modified or mixed polymers of styrene have been made. A resin obtained by the polymerisation of technical styrene exhibited abnormal solubility. Although apparently similar to ordinary polystyrene it had poor solubility. This difference in behaviour was attributed finally to the presence of minute traces of *p*-divinylbenzene. 0·002 per cent of *p*-divinyl benzene is enough to produce insoluble polymers.[30] A process is protected in which a resin is produced which only swells in benzene without actually dissolving. In it styrene is polymerised with 0·05 to 10 per cent of its weight of divinyl benzene.[31]

A tough flexible resin is claimed by heating a solution of styrene with not less than 5 per cent of water.[32] A resin is obtained by heating at 90° C. a solution of styrene and anisole in carbon tetrachloride, with tin tetrachloride as catalyst.[33] Styrene and vinyl α-methyl valeric ester are polymerised together to yield a mixed resin.[34] Mixtures of styrene and methyl, ethyl, butyl, cyclohexyl, cetyl or bornyl methacrylate, or ethylene glycol dimethacrylate, are polymerised together in the presence of sulphur dioxide.[35] Mixed resins are produced incorporating phenol or phenolic bodies with styrene. A resin compatible with wood oil is made from a mixture of styrene, borofluoroacetic acid, monophenylene glycol ether and phenol.[17] An alkali resistant lacquer is obtainable from the product derived by heating styrene and phenolic resin in the presence of a monohydric alcohol of boiling range above 80° C.[36] Polystyrene may be hydrogenated under the influence of heat and pressure using an aluminium, nickel or cobalt catalyst. Hydrogenation is said to confer heat resistance.[37] Styrene is polymerised with diene compounds such as butadiene or dimethylbutadiene.[38] Styrene and vinyl esters, including vinyl chloride,[39] or unsaturated ketones[40] may be co-polymerised to yield resins. Maleic anhydride and styrene can be reacted together to yield resinous substances.[41] Hard resins are obtained by polymerising styrene in the presence of small percentages of chlorinated

diphenyl.[42] Substituted styrenes such as *o* and *p* methylstyrenes and *o*-hydroxystyrene polymerise to yield resins.[43]

Properties and Uses

Polystyrene resins have not, as yet, enjoyed any great popularity in the varnish trade, and this may be attributed in part, at least, to their high price. They possess, however, certain excellent properties, and it can be predicted safely that they will find a permanent niche for themselves in lacquers for special purposes.

Solubility.—Polystyrene resins are clear, water-white solids, soluble in aromatic and chlorinated hydrocarbons and some ketones and esters, but insoluble in aliphatic hydrocarbons, glycol ethers, and alcohols, including cyclohexanol.[44]

Plasticisers.—Their flexibility can be improved by the addition of plasticisers among which may be included dibutyl phthalate, diphenyl phthalate, chlorinated diphenyls, benzyl, dibenzyl, methylbenzyl, dimethylbenzyl, phenylethyl, cyclohexyl and chlorinated benzyl derivatives of tetrahydronaphthalene, ethylacetanilide, camphor, triphenyl, tritolyl, and tricresyl phosphates, benzyl and methylbenzoyl benzoates, tributyl and triamyl citrates, ethyl and butyl oleates, butyl stearate, dixylylethane, glycerol dibenzyl ether, diphenylpropane, cresol, or maleic anhydride-castor oil reaction products.[45]

Thermoplasticity.—Polystyrene resins are thermoplastic and this property enables them to be used for injection and pressure moulding. They may be applied also to form an outer coating on wire by extrusion processes.

Electrical Properties.—Polystyrene resins have excellent insulating properties which are claimed to be comparable with those of mica and superior to those of shellac. Ellis states that polystyrene has greater insulating power than any other synthetic resin. Matheson and Goggin have studied the effect of film thickness on the dielectric strength of polystyrene films. When it is necessary to plasticise polystyrene, hydrocarbon plasticisers such as diphenyl naphthalene are recommended in order not to diminish its electrical properties. This contention is supported by Staudinger and Stanley, who record that plasticisers containing the elements carbon and hydrogen only do not impair the electrical properties of polystyrene. Plasticisers containing polar groupings like oxygen diminish electrical properties.

An insulating composition is claimed from a mixture of chlorinated naphthalene and 1 per cent of polystyrene.[46]

Water Resistance.—Polystyrene can be used in water resistant lacquers because of its very low water absorption. If plasticisation is necessary, a careful choice of plasticiser should be made to prevent impairment of the water resistance.

According to some workers, the water absorption of films is substantially proportional to the polarity of their constituents. Polystyrene

has good water resistance and is non-polar. Polystyrene has better water resistance than benzyl and ethyl cellulose, nitrocellulose, cellulose acetate or cellophane, the water absorption increasing in this order.[47]

Chemical Resistance.—Polystyrene has good chemical resistance, being resistant to acids, alkalis and salts. Resistance to hydrofluoric acid is claimed.[48] A sea-water and alkali resistant lacquer is made from polystyrene plasticised with dibutyl phthalate.[49]

Durability.—To obtain the best durability from polystyrene the addition of plasticisers is necessary. Korzhavin ascribes the ageing of polystyrene films to loss by evaporation of low boiling polymers. He suggests a method of formation for a resin in which volatile constituents are absent, by polymerising styrene under a slowly rising temperature (from 40°–160° C.). The heating may occupy from fifteen to twenty days and the resultant product is heated for four hours under vacuum at 170°–175° C.[50]

Adhesion.—The adhesion of metal lacquers is improved by the addition of coumarone resin, and the following mixture comprising polystyrene, ten parts, coumarone, seven parts and dibutyl phthalate, five parts in suitable solvent, is suggested.[49]

Special Uses.—Lacquers based on polystyrene have been used as media for luminous paints. They are used with pigments such as the sulphides of strontium, calcium, zinc, rubidium and bismuth.[51]

Other uses for polystyrene resins include the manufacture of lacquers for metal, media for light resistant lacquers and enamels, impregnating solutions for fabrics, dope for aircraft, special floor lacquers, emulsions for various purposes, and adhesives.

An aircraft dope is made from polystyrene, vinyl chloride, and chlorinated diphenyl dissolved in a mixture of ethyl acetate and acetone.[52]

Heat resistance of polystyrene can be improved by making certain additions. Among the additions effecting this improvement may be included acrylo or methacrylonitrile, alkyl phenols, thiophenol, phenol sulphides and disulphides.[53]

Application.—Polystyrene lacquers may be applied by brushing, dipping or spraying, depending upon the solvents used and other constituents present, but there is a distinct tendency to cob-webbing. Adhesive coatings may be obtained on metals by cataphoresis.[54]

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Vinyl Resins

Organic Vinyl Ester Resins

Vinyl esters readily undergo polymerisation to yield resinous products. Among the organic vinyl esters recorded in literature, may be included, the acetate, propionate, butyrate and mono and trichloracetates.

Polymerisation of Organic Vinyl Esters

Effect of Light and Temperature.—Vinyl acetate resins which are simple polymerisation products of vinyl acetate are the most popular of organic vinyl ester resins. Monomeric vinyl acetate (b.pt. 73° C.) polymerises in the cold when exposed to light. If the influence of light is removed polymerisation can be effected by raising the temperature. The presence of air or oxygen seems to be essential for heat polymerisation unless temperatures considerably in excess of 100° C. are used.[1]

Peroxide Catalysts.—Peroxides have a catalytic effect on the rate of polymerisation of vinyl acetate. Meunier and Vaissiere [2] claim that commercial vinyl acetate contains small amounts of peroxide and these accelerate polymerisation in closed vessels. Benzoyl peroxide (0·1 per cent) has been suggested as a suitable catalyst.[3] Mixed peroxides of succinic and stearic acids or of adipic and lauric acids have been used.[4] When fatty acid peroxides are used as catalysts they are claimed to yield highly polymerised products with good solubility.[5] Other catalysts include acetyl benzoyl peroxide (0·15–0·3 per cent), ozone, ozonides and uranyl nitrate, copper metal precipitated on silica gel, Kieselguhr, Florida earth, boron trifluoride, lead tetraethyl, hydrochloric acid, the reaction product of acetic anhydride and sodium perborate, the reaction products of aliphatic anhydrides and hydrogen peroxide or sodium peroxide,[6] and aqueous solutions of calcium or barium peroxides.[7]

Catalyst Assisters.—Addition of ammonia, hexamethylenetetramine, oxides of zinc or magnesium, sodium hydroxide, or borates and phosphates of the alkaline metals to aqueous solutions of calcium or barium peroxide greatly improve their catalytic effect.[7]

Water is claimed to have a stimulating influence upon benzoyl peroxide when this is used as a catalyst. At 100° C., under pressure, using benzoyl peroxide, the addition of water improves the yield of polymerised vinyl acetate from 55 to 80 per cent.[8] Yamada,[3] however, states that the presence of water has an undesirable effect. Polymerisation of vinyl acetate or chloride is effected by heating at 40° C. with benzoyl peroxide

and catalyst-assisting metals such as aluminium, tin or lead.[9] Acetyl benzoyl peroxide is said to be a better catalyst than benzoyl peroxide.[10]

The application of pressure facilitates the polymerisation of vinyl acetate and enables lower temperatures to be used.[11] Stirring increases the speed of reaction.

Polymerisation Inhibitors.—Polymerisation of vinyl acetate under cold conditions by the action of light is inhibited by the presence of oxygen.[12] The retardation of photopolymerisation is stated to be due to absorption of atmospheric oxygen.[2]

Antioxidants such as sulphur may prevent the normal polymerisation of vinyl esters. Their influence may be eliminated by the addition of benzoyl peroxide.[13]

Polymerisation in Presence of Solvents.—The polymerisation reaction is exothermic and may become violent. It is more easily controlled if it is conducted in the presence of a solvent. Among solvents suggested are, dichloroethylene, trichloroethylene, toluene, benzene, alcohols, butyl and ethyl acetates, methyl ethyl ketone, ethyl dichloride, chlorobenzene, petroleum ether, ether, and di-*n*-butyl ether, chloroform, acetone, cyclohexane and cyclohexanol.[14]

Adjustments in Method.—The violence of the reaction is more easily controlled if water is added during polymerisation. If water is added in the late stages of the polymerisation, harder resins result.[15]

To produce a vinyl ester resin insoluble in toluene, the polymerisation is conducted below 60° C. in a solvent whose solvent power is similar to that of toluene.[16]

Aeration of polymerised vinyl acetate is removed by warming the product to soften it, under an inert liquid like water, castor oil, hydrocarbon oils or alcohol, and applying pressure.[17] Clarification of solutions of vinyl resins is effected by adding an acidic coagulant to cause coagulation of colloidal suspended matter which is removed by filtration. Coagulants include succinic, salicylic, phosphoric, tartaric, citric and lactic acids.[18]

Modified Vinyl Ester Resins

Modified vinyl ester resins, in addition to mixtures of acetate and chloride which are discussed at greater length later, are recorded. Vinyl esters have been polymerised in the presence of polymerised fatty oils. Vinyl acetate is polymerised in the presence of non-oxydised drying oils, e.g. a mixture of raw linseed oil and vinyl ester in toluene is polymerised using benzoyl peroxide as catalyst.[19] A modified resin is made by admixture of styrene with a vinyl ester of an aliphatic carboxylic acid.[20]

During the polymerisation of vinyl acetate on the commercial scale, traces of a polymer are formed which are insoluble in the usual organic solvents.

Replacement of the acetate radical in polyvinyl acetate is accomplished by heating with acids. When a solution of polyvinyl

acetate in benzene is boiled with formic acid, acetic acid can be boiled off. Butyric acid can be used in place of formic acid.[21] Rosin, Manila copal, naphthenic, stearic, ricinoleic, citric, tartaric and lactic acids can be treated thus. The rosin compound is miscible with linseed oil.[22]

Extraction of vinyl chloride or vinyl acetate products with solvent permits the removal of low molecular weight polymers. Suitable solvents include benzine, alcohol and aliphatic ethers.[23]

Inorganic Vinyl Ester Resins

Vinyl halides (chloride and bromide) polymerise under the action of heat in the presence of catalysts, or under the action of light.

Polymerisation Catalysts.—Catalysts assisting polymerisation by light include salts of cobalt, nickel, copper, manganese, uranium and vanadium. Catalysts assisting heat polymerisation of vinyl chloride include benzoyl peroxide, barium peroxide, ozone, trioxymethylene, lead tetraethyl, and hydrochloric acid. Waterman, Laendertse and Colthoff have suggested aluminium chloride as a suitable catalyst.[24]

Hydrogen peroxide is claimed as a very good catalyst for polymerisation of vinyl bromide.[25]

Like vinyl acetate the polymerisation of vinyl chloride can be conducted in solution and has also been conducted under pressure.

Polymerisation is retarded by iron or bronze [25] but accelerated by glass.

A polymerised vinyl chloride which is insoluble in methylene chloride can be depolymerised by heating with an acid or acid salt to become soluble in methylene chloride.[26]

Modified Vinyl Ester Resins

Modifications of vinyl resins have been recorded. Thus vinyl chloride has been polymerised with formaldehyde, acrolein, unsymmetrical dichlorethylene, trichlorethane, or butadiene and an oxidising catalyst.[27] A resin which, on further heating, will yield an infusible film is obtained from a mixture of polymerised vinyl chloride and a partly polymerised alkyd resin. The alkyd resin is comprised of glycerol, ethylene glycol, phthalic anhydride and adipic acid.[28] Polyvinyl esters can be reacted with drying oil stand oils to yield air drying, non-yellowing, water, alkali and light resistant films.[29]

Mixed Organic and Inorganic Vinyl Ester Resins

These are very popular combinations. The esters may be polymerised together under the same conditions as used for polymerisation of the individual esters. A resin formed by co-polymerisation in this way, contains both components chemically combined in the resin molecule, and so differs from a simple mixture. Vinyl chloride and a vinyl ester of a lower fatty acid are polymerised together. A mixed vinyl

resin which is substantially insoluble in toluene is made by polymerising vinyl chloride 4 parts and vinyl acetate 1 part, in the presence of benzoyl peroxide. A resin suitable for baking on rubber is obtained by polymerising a mixture of vinyl chloride (80–90 per cent) and vinyl acetate.[30]

Vinyl chloride and vinyl acetate are mixed together in butane in a lead-lined autoclave and heated to 30° C. in the presence of acetyl benzoyl peroxide. Since butane is a solvent for the monomers but a non-solvent for the polymers, the former are readily separated from the latter by filtration. If during the polymerisation reaction the polymers are removed as quickly as they are formed, and this is possible because of their insolubility in butane, then the concentration of monomers can be kept constant.

Properties of Vinyl Acetate and Vinyl Chloride Resins, including Mixed Resins

Vinyl ester resins are very pale in colour, being normally water white. They possess a faint sweet smell or are completely odourless, and they soften on heating. They are not extensively used as yet in varnish and lacquer manufacture although they have special applications. Lilley [32] attributes the slow growth of interest in vinyl ester resins to the following factors : they yield solutions of high viscosity and they require expensive solvents, they are costly in themselves and have poor exterior durability. Further, they tend to disintegrate under the influence of heat or light.

Solubility.—Vinyl acetate resins are fairly soluble in low molecular weight alcohols, but more rapid solution is attained using mixtures of alcohol containing 5 per cent water or turpentine.[33] They are soluble in low molecular weight esters but are insoluble in both high molecular weight esters and alcohols. Other solvents include aromatic hydrocarbons, acetone, methyl ethyl ketone, anisole, chloroform, aniline, and nitrobenzene. Other non-solvents include petroleum hydrocarbons, and ether. Vinyl chloride resins are soluble in chlorobenzene, acetone, methyl cyclohexanone, mesityl oxide, tetrahydrofurfuryl alcohol and toluene, although their solubility is dependent upon the molecular weight of polymer present.

For vinyl acetate-chloride resins, Doolittle [34] states that the best solvents are ketones and that hydrocarbons are merely diluents. Esters, ethers and alcohols are said to cause precipitation or gelation. A lacquer is made from a mixed vinyl resin by dissolving it in a mixed solvent comprising dipropyl ketone and methylisobutyl ketone with a hydrocarbon diluent.[35]

Plasticisers.—Plasticisers for vinyl resins include Cetamoll QU, Clophen A 60, Desavin, tributyl, isobutyl, cresyl and phenyl phosphates ; phthalates, Palatinols BB, C, HS, L and O ; Plastomoll S.W., T oil, Vulkanol B, dibutyl and amyl tartrates, triacetin, diallyl succinate, triallyl citrate, β-chlorethyl phthalates, succinates, or maleates, esters

of cyclohexene-4, 5-dicarboxylic acid, acetophenone, toluene sulphonamides, and glycollates. Dodecyl linoleate and coconut alcohol esters of elaeostearic acid, dicetyl phthalate, organic sulphones and aliphatic esters of diacetoxystearic acid, are plasticisers for polyvinyl chloride resin.[56]

Plasticised polyvinyl chloride pastes are made by dissolving into a suitable ester plasticiser by heating, amounts of polyvinyl chloride until the plasticiser content is 38–80 per cent by weight of the final product. The temperature of solution is maintained below 70° C.[57]

The Action of Light and Heat.—Much has been published concerning attempts to prevent disintegration of vinyl resins by light and heat. Discoloration by light is stated to be prevented by adding to the vinyl resin a phenolic compound having one hydroxyl group and an ortho alkyl substituted carboxyl group. Other light stabilising agents which are mixed in small amounts with the resins are resorcinol disalicylate, resorcinol dibenzoate, phenyl phthalate, phenyl benzoate, *o*-tolyl benzoate, *o*, *m* and *p*-tolyl salicylate.[36]

Incorporation of light stabiliser (1–5 per cent) can be effected by milling in the resin at 110° C. Alternatively, stabiliser and resin may be precipitated from a solution in a suitable solvent by addition of water. Stabilisers which may be incorporated by these methods are given as eugenol, guaiacol, *o*-nitrophenol, *o*-nitraniline, triethylene glycol salicylate and ethylene glycol monobutyl ether salicylate. When these materials are added in larger quantities they may serve as plasticisers.[37]

When vinyl resins are heated in the presence of iron or its compounds discoloration may occur.

Zinc and tin surfaces also cause decomposition of vinyl resins on stoving, with elimination of hydrochloric acid.[34]

Vinyl chloride resins do not decompose on phosphatised iron surfaces.[38] Inhibitors of such discoloration include urea, methyl urea, urea oxalate, thiourea, diethyl thiourea, triethanolamine, dipropanolamine, benzylamine, dibenzylamine and triamylamine.[39]

An inorganic lead compound capable of forming insoluble chlorine compounds is added to a mixed vinyl halide-vinyl acetate resin to prevent decomposition by heat. Other heat stabilising agents for the mixed resin are aluminium, cadmium, magnesium, cadmium sulphide and sulphite, cerium sulphite, sodium sulphite, strontium sulphite and manganese silicate; 0·5–3·0 per cent calculated on the resin, of lead and tin stearates or oleates, or organic compounds of lead and tin such as Pr_4Pb, Pr_4Sn, Ph_4Pb, Ph_4Sn, $PrPbPh_3$, Pr_2SnPb_2, Pr_3PbPh, Ph_3PbOH, Ph_2PbO, Ph_3SnOH, Ph_2SnO, $PrPh_2PbOH$, $PrPh_2SnOH$.[40]

Heat stabilisers which have either a slight reducing action or which form insoluble chlorine derivatives are oxides of antimony, bismuth, copper and mercury; sulphites of silver and calcium, silicates of copper and magnesium, metallic copper, mixtures of lead sulphite and basic lead sulphate and sublimed blue lead. Heat and light stability is accomplished by polymerising vinyl chloride in the presence of small

amounts of acids such as acrylic, methacrylic, itaconic or maleic acids. The resultant products are treated with a dilute solution of alkali. Other stabilising agents are glycerine, leucine, alanine, glue, gelatin, asparaginic, *o* and *p* amino benzoic and sulphanilic acids. Blends of vinyl chloride and acetate are stabilised by the addition of hexamethylene tetramine; salts of weak acids with cadmium, lead, manganese, alkali or alkaline earth metals, the weak acid radicals including stearates, palmitates, oleates, ricinoleates, abietates, linoleates, laurates, acetylated ricinoleates, and oxidised ricinoleates. Copper oleate, butyl and methyl salicylates are also used.[41]

Adhesion.—Adhesion of mixed resins is improved by polymerising vinyl chloride and vinyl acetate with acetyl benzoyl peroxide in the presence of 1 per cent of allyl crotonate, ethylene glycol dicrotonate, divinyl ether or divinyl acetal.[42] The adhesion of air-dried coatings is not outstanding, but stoving produces improvement. Polyvinyl acetate has good adhesion, but polyvinyl chloride has poor adhesion. A mixed resin is an improvement.[43]

The Relation of Resin Properties and Molecular Weight.—Vinyl resins have high molecular weights. The molecular weight distribution of vinyl ester polymers is determined either by solvent extraction, fractional precipitation or by means of the ultracentrifuge. Information on fractionation and size distribution in vinyl acetate polymers has been given by Blease and Tuckett.[53] The extent of polymerisation has an important bearing on the physical properties of the resin. Properties such as elasticity, tensile strength and impact strength, increase rapidly with molecular weight at low molecular weights, but the increase is not so marked at higher molecular weights.

Other properties such as refractive index, hardness and water absorption appear to be independent of molecular weight.[44] As the degree of polymerisation increases solubility decreases, but viscosity and melting-point increase.

Other Properties.—The function of vinyl acetate in mixed resins improves compatibility and solubility.[34]

The possibility of film imperfections such as formation of ridges during drying is prevented by the addition of from 2 to 12 per cent of a polyhydronaphthalene to a solution of the resin in a solvent. The addition of tetrahydro, decahydro, dihydro, hexahydro and octahydronaphthalenes has been suggested for this purpose.[45]

Uses

Vinyl resins are useful constituents of acid and alkali resisting lacquers. They may be used in paper varnishes which are likely to come into contact with alkaline materials like liquid soap solutions, shampoos, etc. Their pale colour and very weak smell make them a possible choice for the production of odourless spirit paper varnishes. A recent use for polyvinyl resins is in the manufacture of sleeving for wire, for the resins

have the chemical, electrical and mechanical properties necessary. Flexibility can be improved by addition of plasticiser. Vinyl chloride resin coatings are fire resistant.

Douglas [46] observes that vinyl resins as wire coatings are more chemically inert than rubber and do not cause corrosion of the wire. Lacquers made from them are suitable for use in electrolytic plants because they are unaffected by salt solutions. Vinyl resins in combination with other constituents may be used in the production of dopes for aircraft fabric. Polyvinyl chloride in amounts of not less than 5 per cent. is suggested, and this may be incorporated with three different types of dope ; with tricresyl phosphate, in ethyl acetate and toluene ; with chlorinated diphenyl and polystyrene in ethyl acetate and acetone ; or with polyvinyl acetate and castor oil in toluene and benzene.[47] Other uses of vinyl resins include media for metallic lacquers because of the very low acidity of these resins ; media for luminous paints, anti-shatter lacquers for glass ; lacquers for electric light bulbs ; nitrocellulose lacquers ; printing inks ; moisture resistant lacquers for cellophane comprising vinyl resin, plasticiser and paraffin wax ;[48] adhesives for paper, fabric, celluloid, glass, leather or metals ; lacquers for the inside of food or beverage containers ; media for wall paints resistant to plaster, and moulding compositions.

Polyvinyl Acetal Resins

These are the reaction products of aldehydes and polyvinyl alcohol in the presence of acid catalysts. Aldehydes used include formaldehyde, acetaldehyde, benzaldehyde, acrolein, aldol, butyraldehyde and glyoxal.[49] Aldehydes containing from 2–18 carbon atoms are reacted with polyvinyl alcohol in the presence of sulphuric acid to yield resins suitable for a variety of uses.[54] Mixed aldehydes may be used. Polyvinyl acetal resins can be produced without the necessity of isolating polyvinyl alcohol. Polyvinyl acetate, para-acetaldehyde and formaldehyde are dissolved in a mixed solvent consisting of ethyl acetate and ethyl alcohol. The reaction products are then maintained at 40° C. in the presence of sulphuric acid for approximately 150 hours, to yield an acetone soluble resin.[50] Polymerised vinyl ester, during or after partial hydrolysis, is reacted with an aldehyde in the presence of a mineral acid.[51]

Solvents for these resins are hydrocarbons, chlorinated hydrocarbons, ketones, alcohols and esters.

Durable films resistant to light are obtained by adding monocresyl diphenyl phosphate to polyacetal resins. The product of hydrolysed polyvinyl acetate and formaldehyde can be plasticised with dimethyl phthalate to yield a tough, flexible adhesive suitable for safety glass.[52]

Careful choice of plasticiser is necessary for the best results with polyvinyl acetal resins, and mixtures of dilauryl phthalate and diethyleneglycol ; dilauryl phthalate and dibutyl glycollate ; phenyl ethyl alcohol and dibutyl diglycollate ; phenyl ethyl alcohol and dibutyl phthalate ; or phenyl ethyl alcohol and diethylene glycol dibutyrate.[55]

These resins have not, as yet, assumed any great popularity in the varnish trade and their value to it is still in the process of assessment.

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Polyacrylic and Polymethacrylic Resins

Acrylic acid, methacrylic acid, esters of these acids and other acrylic derivatives, such as chlorides, nitriles and amides, polymerise readily. Of these compounds the esters of acrylic and methacrylic acids yield the resins which are of importance to the varnish industry. The methyl and ethyl esters are the most important. Copolymers of these esters also yield valuable resins.

Esters which undergo Polymerisation.—Resinous materials have been made by the polymerisation of the following esters: ethyl acrylate, methyl acrylate, methyl methacrylate, ethyl methacrylate, isobutyl methacrylate, octadecyl methacrylate, *n*-propyl methacrylate, *n*-butyl methacrylate, capryl acrylate, cetyl acrylate, decyl acrylate, α-ethyl hexyl acrylate, and the methacrylate esters of glycol and glycerol.[1]

Mechanism of Polymerisation Reaction.—The mechanism of the polymerisation reaction of esters of acrylic and methacrylic acids or of the acids themselves has been studied by Flory, Staudinger and Kohlschütter, Goodeve, Monnier, Suoz and Briner, Hibben, Norrish, Melville and others. Ellis also provides information on this subject.[2]

Factors Influencing Resin Formation

Light and Heat.—Polymerisation of acrylic and methacrylic esters occurs under the influence of light and heat, with or without added catalyst.

Photochemical polymerisation of methyl methacrylate in the form of vapour may be effected if the radiation is greater than 2200 Å. Polymerisation continues in the absence of light if the ester is subjected to sufficient initial irradiation.[3] According to Strain,[4] for the polymerisation of methacrylic esters in solution, high temperatures accelerate the rate of polymerisation and shorten the induction period. The higher the temperature of polymerisation the lower the molecular weight of the polymers formed.

Solvents.—Polymerisation may be conducted on the ester either alone or in solution. Better control of polymerisation is claimed if a solvent is used. The solvent used may be a solvent for the monomer but a non-solvent for the polymer. Or polymerisation may be conducted on a dispersion of the monomer in a non-solvent.

Solvents which have been used for polymerisation include acetone, ethylene chloride, butyl acetate, methoxyethanol, and dioxane. Solvents vary in their effect on the polymerisation rate, and according to Strain, *loc. cit.*, polymerisation is slow in acetone, ethylene chloride and butyl acetate but more rapid in dioxane and methoxyethanol. Further, the

rate of polymerisation is directly proportional to the concentration of monomer in the solvent.

Blends of methanol and water are also used as media for polymerisation and in this case the polymers will separate as formed. Paraffin oil or a mixture of this with benzine is used with the same object. The monomer is soluble in the solvents but the polymer is precipitated.[5]

The monomer may be dispersed as an emulsion in a non-solvent like water and then polymerised.[6]

Catalysts.—Catalysts may be present and these include oxygen, ozone, benzoyl peroxide, hydrogen peroxide, a mixture of benzoyl peroxide and hydrogen peroxide, sulphur dioxide, sulphurous acid, water soluble sulphites and hyposulphites, benzoic acid, Tetralin peroxide, and benzaldehyde.[7]

It has been recorded that with esters of methacrylic acid the presence of oxygen seems essential for polymerisation, for even at 65° C. in absence of both oxygen and light no polymerisation occurs. Benzoyl peroxide is a very efficient catalyst, 0·1 per cent being all that is necessary for polymerisation of methyl methacrylate at 65° C. At lower temperatures in the absence of light, it becomes more or less inactive.[4] Slow polymerisation of methyl methacrylate occurs in the absence of catalyst but Norrish and Brookmann consider this to be due to the presence of adventitious catalysts.[8]

Some processes include the use of pressure to assist polymerisation.[9]

Manufacturing Methods

Various methods used in the production of polyacrylic resins are recorded as follows :—

A mixture of ethyl methacrylate (57 kilos) and benzoyl peroxide (250 grm.) is heated at 100° C. for several hours to yield a hard resin. Other processes use a temperature range of 60°–100° C.[10]

A resin is obtained by heating a solution of ethyl acrylate in acetone, in the presence of oxygen or a compound capable of evolving oxygen.[11]

Polymerised methyl methacrylate is obtained in pulverent form by heating a stirred mixture of methyl methacrylate (2 pts.), methyl alcohol (16·3 pts.), water (81·7 pts.) and benzoyl peroxide (0·02 pts.) at 65° C. for twenty-four hours. Alternatively, the resin is obtained as a fine spongy mass by heating a mixture of methyl methacrylate (20 pts.), water (40 pts.) and methyl alcohol (40 pts.) at 65° C. for four days. A similar process in which methyl methacrylate is polymerised in aqueous methyl alcohol describes the product as a light fluffy powder.[12]

If polymerisation of acrylic derivatives is conducted in the presence of previously prepared polymers, only small traces of catalyst (0·003 per cent) are necessary and the process yields bubble-free resins at 50°–60° C.[13] Polymerisation of acrylic esters or their homologues may be conducted in presence of water soluble salts or of mixtures of solvents and plasticisers.[14] Polymethacrylic acid acts as a granulating agent

when methyl methacrylate is polymerised in an aqueous medium, using benzoyl peroxide as catalyst. Resins may be obtained in a granular form by heating until plastic and kneading them in this condition.[15]

A resin is obtained by boiling a mixture of ethyl acrylate, sodium borate and glacial acetic acid in acetone.[16]

An emulsion of methyl methacrylate is flowed through a heated tube to effect polymerisation. The rate of flow is such that turbulent motion is caused.[17]

Polyacrylic or polymethacrylic esters are obtained free of monomer by extracting a dispersion in water with a water miscible solvent.[18]

It has been indicated already that polymerisation in solvent permits control to be exercised. The presence of up to 1 per cent of an unsaturated terpene compound is stated to prevent inconveniently violent reaction during polymerisation of ethyl methacrylate.[19] Effective terpene compounds are rosin, turpentine, pine oil and melissa oil.

Polymerisation Inhibitors.—The polymerisation of acrylic and methacrylic esters can be inhibited by the presence of certain compounds. These inhibitors may be used to control or stop polymerisation, so as to permit purification of the monomeric ester by distillation. Anhydrous metallic halides which function as inhibitors by combining with any oxygen-containing organic compounds which may be present, include antimony trichloride and pentachloride, arsenic trichloride and pentachloride, aluminium chloride, tin tetrachloride and potassium bismuth iodide. Other polymerisation inhibitors include hydroquinone, tannic acid, pyrogallol, and copper powder.[20]

Modified Acrylic Resins

A polymerised material from acrylic acid nitrile is made by heating an aqueous emulsion. Resins are also obtained from acrylic acid nitrile by polymerisation, after first treating the nitrile at a low temperature with a catalyst such as H_2MnO_4, or $HMnO_4$, or salts of these acids. The manganese compound is removed before polymerisation.[21]

Many modifications of polyacrylic or polymethacrylic esters are made, and these are based chiefly on the co-polymerisation of these esters with other polymerisable compounds. Thus mixed polymers of acrylic esters and styrene are made.[22] Using benzoyl peroxide, benzaldehyde or hydrogen peroxide as catalyst, acrylic acid esters are polymerised with an aqueous solution of polyvinyl alcohol and an amide or metallic salt of polyacrylic acid.[23] Small amounts of divinyl compounds are suggested additions to acrylic acid polymers as cross-linking agents to induce insolubility.[24] Lacquers resistant to solvents are prepared from the co-polymerisation of acrylic esters with 20–40 per cent of acrylonitrile.[25]

A mixture polymerisable by benzoyl peroxide is made by heating together a toluene solution of methacrylic anhydride, fused sodium acetate and a partial phthalate of soya bean oil monoglyceride. The monoglyceride product is derived from soya bean oil by heating the

oil with glycerol in presence of litharge, and reacting the resultant product with more glycerol and phthalic anhydride.[26]

Co-polymerisation of esters of acrylic or methacrylic acid is frequently used to obtain resins with certain properties, which cannot be obtained by simple mixing of the polymers. Resins suitable for lacquers are claimed from the co-polymerisation of ethyl and octadecyl methacrylates. Durable products suitable for coating wire mesh are claimed from the co-polymerisation of methyl and ethyl or octyl methacrylates.[27]

Properties and Uses

The acrylic type resins have many valuable properties, and if it were not for their high price there is no doubt that they would become very popular.

They are water white in colour and vary in condition from hard resins to viscous liquids.

Hardness.—The hardness of the resins is controlled both by the type of acid present and by the type of alcohol in combination with it. With a given acid and alcohol a hard or a soft resin can be obtained by varying the molecular weight of the polymer. The softening point and tensile strength of methacrylic esters decrease with increase in the molecular weight of the alcohol.[7] The following are in order of hardness, commencing with methyl methacrylate which yields the hardest resins of all; methyl methacrylate, ethyl methacrylate, methyl acrylate, and ethyl acrylate. *n*-Butyl methacrylate polymer is soft at ordinary temperatures and lauryl methacrylate polymer is a viscous liquid. The hardness of isobutyl methacrylate is greater than that of the *n*-butyl polymer.[28] The hardness of soft resins can be improved by co-polymerisation with methyl esters.

Yellowing.—Under the action of heat these resins show very little tendency to yellow, neither is there any appreciable yellowing tendency on exposure. At 350° F. no darkening occurs. Polymethylmethacrylate is stated to exhibit no yellowing up to 390° F. but at 660° F. it decomposes to the monomer.[28]

Depolymerisation.—Du Pont de Nemours [7] report that methacrylic ester resins exhibit a very slight tendency to depolymerisation at 480° F., but that 840° F. is necessary to cause complete depolymerisation to the monomer.

Fluidity on Heating.—On heating, methacrylate resins do not immediately become liquid but remain rubbery over a wide range of temperature. Fluidity can be induced, however, by the addition of other resins which act as fluxes.[28] Such resins may be rosin, ester gum, coumarone or damar.

Durability.—These resins have excellent durability and Klein and Pearce, *loc. cit.*, describe how a mixture of methyl acrylate and ethyl methacrylate, after three years' exposure, showed no failure in any direction. There was no yellowing and no loss of gloss. Using a pigment which normally chalks on exposure, a non-chalking enamel can be formulated

from a blend of from one to two parts of nitrocellulose with one part of acrylic resin.[29]

Transmission of Light.—It has been recorded that acrylic or methacrylic ester resins transmit ultra-violet light better than glass. Pfund records, in addition, that these resins are more opaque to infra-red light than glass.[30] It is interesting to observe, however, that a patent is filed for the production of sheeting for the protection of oil paintings based on an acrylic compound which is claimed to be opaque to ultra-violet light.[31]

Extensibility.—Acrylate resins, especially, have excellent extensibility. Polymethyl acrylate stretches 1000 per cent at ordinary temperatures.[28]

Adhesion.—The adhesion of polyacrylic and polymethacrylic resins is generally good, but better adhesion is obtained on metals if the resin is baked in preference to air drying. Gloss and hardness are also improved by baking. Softer polymers have better adhesion than harder types.[28]

Water Resistance.—The resins have good water resistance. Klein and Pearce, *loc. cit.*, state that soft polymers have a lower water resistance than harder polymers, which are resistant to both cold and boiling water. The water absorption of polymethyl methacrylate is stated to be less than 0·5 per cent.[7] The low water absorption of these resins makes them valuable components of waterproofing compositions. The following are examples. Water resistant lacquers are derived from a mixture of chlorinated rubber and polyacrylic esters.[32] A coating for paper is made from a blend of polymethacrylate resin and paraffin wax. It is superior to paraffin wax alone, for water resistance, especially after folding.[28, 33] A film derived from polyacrylic resin alone is also used for waterproofing offset paper.[34]

Acidity.—The acidity of acrylic resins is nil. A medium for luminous lacquer is based on a composition containing methyl methacrylate resin and polystyrene resin.[35]

Film Strength.—Acrylic resins give films which are not so tough as those from methacrylic esters.

Chemical and Solvent Resistance.—The resins have good chemical resistance, being unaffected by dilute acids such as hydrochloric, sulphuric, or phosphoric acids. Hard resins are resistant to acetic acids. The resins, generally, are resistant also to dilute ammonia, dilute caustic soda, ozone and oxygen. They are also resistant to certain solvents such as petroleum hydrocarbons or mineral oils.

Electrical Properties.—Acrylic and methacrylic polymers are very useful for electrical purposes. The breakdown voltage of polymethyl acrylate resin is given as 280,000–340,000 volts per cm. Their power factor is higher than that of polystyrenes.[28] Other facts which make these types of resin invaluable for electrical work have been enumerated, as non-tracking tendency, reduction of power factor with increase of temperature, high melting-point, and resistance to substances likely to be encountered in electrical work such as mineral oils and ozone.[7] It has been suggested that monomers of acrylic or methacrylic esters could

be used as impregnating liquids for coils, rotors, etc., and polymerised *in situ*, with the consequent saving due to the elimination of the loss of volatile solvent which is usual with the ordinary type of impregnating solution.

Defects.—Apart from their high price these resins have certain disadvantages. They exhibit appreciable solvent retention and baking is necessary to obviate this. They have a tendency to pinhole when sprayed. The film never becomes insoluble in many organic solvents even after stoving and is apt to become marred if accidentally contaminated with them.

Solubility.—Acrylic type resins are soluble in a wide variety of solvents, including toluene and aromatic hydrocarbons generally, ethyl acetate, Cellosolve, acetone, cyclohexanone, chlorinated hydrocarbons, anhydrous organic acids and dioxane. As the molecular weight of polymethacrylate resins increases the solubility decreases.

The resins are insoluble in petroleum hydrocarbons, aliphatic alcohols and ethers, glycols, glycerol, vegetable oils, including castor oil, and carbon tetrachloride. *n*-butyl and isobutyl methacrylate resins are more soluble generally than resins of esters from lower alcohols. Thus *n*-butyl and isobutyl resins are stated to be soluble in linseed oil, turpentine or white spirit.[28]

Plasticisers.—Most of the common plasticisers can be used with polyacrylic and polymethacrylic esters. A comprehensive list would include methyl abietate, butyl tartrate, tricresyl phosphate, chlorinated diphenyl, benzyl and butyl benzoyl benzoates, glyceryl tripropionate, diethylene glycol di-isobutyrate, sec. alcohol carbamates,[28] acetins, tributyl phosphate, butyl stearate, methyl carbitol, benzyl-, phenylethyl-, dibenzyl-, methylbenzyl-, dimethylbenzyl-, cyclohexyl-, and chlorinated benzyl-derivatives of tetrahydronaphthalene, diethyl phthalate, dibutyl phthalate and other phthalates, adipates, and mono- or dimeric alkoxy derivatives of methacrylic esters.[36]

Compatibility.—The resins are compatible with many raw materials at present in use in the varnish trade. They may be used with nitrocellulose, modified and unmodified phenol formaldehyde resins, alkyds, chlorinated rubber, interpolymerisation products of vinyl chloride and vinyl acetate, rosin, ester gum, coumarone, damar and maleic resins. Compatibility is usually better with nitrocellulose than with cellulose acetate. It must be understood that the compatibility of the resin varies appreciably with different types of polymer and on the degree of polymerisation. Different acrylic or methacrylic polymers are not generally miscible with each other.

For methacrylate polymers, however, the ethyl derivative is compatible with the propyl; the propyl with the butyl; the propyl with the isobutyl; and the butyl with the isobutyl.[28]

When mixtures are desired, it is preferable to blend the monomers and then polymerise them.

Varnish Constituents

Application.—If suitable solvents are chosen the resins may be applied by brushing, spraying, dipping or by coating machine. They may be deposited electrically on metals. Compositions capable of being applied by this method are made by dispersing a mixture of methyl methacrylate and butyl methacrylate in hydrophobic mineral oils.[37]

Special Uses

The following compositions from acrylic type resins have been suggested. Polymethyl methacrylate resin is mixed with coumarone and phenol formaldehyde resin or an alkyd.[38] Polymethyl methacrylate resin is blended either with an alkyd or nitrocellulose.[39] A mixture of polyacrylic ester and polyacrylnitrile dissolved in a suitable solvent yields a medium for stoving enamel. The solvent mixture comprises cyclohexanone, dioxane, monochlorbenzene, dichlordiethyl ether and ethylene glycol diacetate.[40] A blend of polyacrylic ester with polyacrylic acid and quartz dust provides an anticorrosive coating for cables. A small amount of β-naphthol may be added.[41]

Acrylic type resins may be used for many purposes, including impregnating insulating compositions, media for luminous paints, clear lacquers for metal, especially aluminium and chromium, lacquers for wood, paper and fabrics ; oil and petrol resisting lacquers for storage tanks, as aqueous emulsions for leather finishing or for overcoming the porosity of bricks, for cellulose lacquers, in chlorinated rubber paints, in oleo-resinous paints, adhesives for fabrics, leather, etc., in lacquers for beverage and fruit juice containers, in boat finishes, in lacquers for rubber, in finishes for lamps and lampshades, in fume resistant lacquers and chemical resistant coatings, in cements for laminated glass, and in gas-impermeable impregnating compositions for fabric.

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Chlorinated Diphenyls

Chlorinated diphenyls do not fall into any one class of varnish constituent, for the lower members are liquids and may be regarded as plasticisers, and the higher members are solids and resemble resins.

Composition and Constitution

They are the simple chlorination products of diphenyl in which the available hydrogens are replaced by halogen. Monochlorodiphenyl contains 18·8 per cent chlorine and decachlorodiphenyl, 71·1 per cent. Intermediate compounds contain the following percentages of chlorine, di- 36·8, tri- 41·4, tetra- 48·6, penta- 54·4, hexa- 59·0, hepta- 62·8, octa- 65·9, and nona chlorodiphenyl- 68·8. Chlorinated diphenyls are not always simple or mixed chlorinated diphenyls, but may contain some high boiling complex compounds such as the chlorination products of ditolyl and dixylyl, incorporated to obtain modifications in properties.

Chlorinated diphenyl products are available under the two trade names of Arochlor and Clophen. Work on the chemical constitution of individual chlorodiphenyls has been conducted by Van Roosmalen.[1]

Formation.—Chlorinated diphenyls are synthesised chiefly by two methods. The first and most important is the direct chlorination of diphenyl in the presence of a catalyst. The other consists in the condensation of chlorinated aromatic compounds such as chloro and *p*-dichloro benzenes.

The experimental results of Andrianov[2] on the chlorination of commercial diphenyl are interesting. Dry chlorine is passed into diphenyl at 100°–200° C., in the presence of iron shavings. The table below gives the properties of chlorinated diphenyls obtained after purification.

Formula.	B.Pt. (20 mm.).	S.G. (20° C.).	Vis. (Centipoises at 100° C.).	M.Wt.
$C_{12}H_9Cl$	160°–170° C.	1·1542	2·0	—
$C_{12}H_8Cl_2$	175°–193° C.	1·2631	3·8	—
$C_{12}H_7Cl_3$	195°–205° C.	1·3589	4·5	—
$C_{12}H_6Cl_4$	220°–245° C. (48 mm.)	1·4568	7·2	—
$C_{12}H_5Cl_5$	—	1·5304	10·2	—
$C_{12}H_3Cl_7$	m.pt. 25° C.	—	19·3	—
$C_{12}H_2Cl_8$	m.pt. 45° C.	—	86·5	—
$C_{12}HCl_9$	—	—	—	441
$C_{12}Cl_{10}$	m.pt. 217°–220° C.	—	—	—

Catalysts.—The catalysts used for direct chlorination include iron, iodine, antimony chloride, a mixture of sulphur and antimony trichloride, and phosphorus chloride.[3] When iron is used as a catalyst the products obtained are dark in colour, a defect which is not associated with the use of iodine.

Manufacturing Methods.—Molten diphenyl is chlorinated in the presence of an iron catalyst by the passage of chlorine. The introduction of chlorine into the molecule results in the evolution of heat and cooling is necessary. Hydrochloric acid is evolved simultaneously. In some processes rigid control of temperature is exercised throughout, different temperatures being used for different stages of the chlorination. Increase in temperature assists in the formation of the higher members of the series. The reaction is sometimes conducted in the presence of solvents of which aromatic and chlorinated aromatic hydrocarbons have been used,[4] or diphenyl is chlorinated after dissolving in a liquid mixture of higher chlorinated diphenyls.[5]

Considerable darkening of the product occurs in the presence of iron when iron is used as a catalyst or as the metal of the reaction vessel. This is overcome by utilising iodine as a catalyst and glass or glass-lined vessels. Alternatively the dark products may be distilled. Chlorinated diphenyl resins, comprising a mixture of chlorinated diphenyl and other diaryl complexes, are subjected to distillation to yield pale products.[6, 11]

The increase in specific gravity which parallels extent of chlorination is used as a means of process control.

Properties

Chlorinated diphenyls vary from viscous colourless oils to pale straw resins. They possess a pleasant, almost imperceptible odour. Among their chief characteristics are stability, excellent solubility and compatibility, neutrality and non-inflammability.

The semi-solid chlorinated diphenyls are difficult to handle. Products which remain fluid at all normal temperatures can be made by preparing concentrated solutions in aromatic hydrocarbons.

Stability.—Stability implies resistance to chemicals, and it is claimed that these materials are unaffected by boiling 10 per cent caustic soda. Resistance to acids is good also and continued heating at 150° C. causes no decomposition. There is no corrosive action on metals. Mild steel after exposure at 325° C. for over 800 hours reveals no pitting.

Chlorinated diphenyls are very resistant to the action of light and have been used to prevent the yellowing of oils during drying.[7] Resistance to disintegration by light diminishes with increasing chlorine content. Chlorinated diphenyls are non-oxidisable.

Solubility.—By reason of their chemical constitution, chlorinated diphenyls are readily soluble in most organic solvents, including aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, turpentine, pine oil, esters, ketones, ethers and glycol ethers, higher alcohols and organic acids. They are insoluble in the lower alcohols, glycerol and water. The solubility of chlorinated diphenyls decreases with increase of viscosity.

Compatibility with most common varnish and lacquer constituents is excellent. They blend thoroughly with drying oils whether untreated, polymerised or oxidised, castor oil, and with kauri, ester gum, rosin, damar, coumarone, vinyl resin, phenol formaldehyde resins, polystyrene resin, chlorinated rubber and asphaltums. They may be used with nitrocellulose but care is necessary in formulation. Satisfactory lacquers are made with benzyl cellulose. Chlorinated diphenyls are compatible with small amounts of many waxes such as paraffin, japan, beeswax, montan, carnauba, ceresin, and ozokerite.[8]

Neutrality.—The acidity of these products is zero and thus they may be used with all basic pigments. Crystalline chlorinated diphenyls are used to prevent livering of pigments.[9]

Toxicity.—They are not considered toxic at normal temperatures. At higher temperatures exposure to the vapour has an irritant effect and precautions should be taken. Continuous bodily contact is said to cause skin eruptions. It is recommended that hands are cleansed thoroughly before partaking of food.

Inflammability.—These products have excellent resistance to combustion due to the presence of chlorine. The lower chlorine content diphenyls can be made to burn, but inflammability decreases as the chlorine content increases. The higher members can be classified as non-inflammable.

Crystallisation.—Pure individual chlorinated diphenyls have a strong tendency to crystallise, a defect which would render them unsuitable for general use. Adjustments in manufacture have been made to render them permanently non-crystalline. High boiling complex compounds formed during the synthesis of diphenyl are added in definite proportions to diphenyl before chlorination, yielding permanently fluid products.

Such high boiling compounds include ditolyl and dixylyl.[10] Alternatively, the diphenyl and high boiling complexes may be chlorinated separately and mixed subsequently. Sometimes chlorinated products derived from the high boiling complexes above are used as raw materials for lacquers.[11]

Penning attributes the fluidity of the lower chlorinated diphenyls to the presence of isomeric forms.[12]

Adhesion.—Adhesion is generally excellent, especially to glass and metal. Lacquers based on chlorinated diphenyls have been suggested for duralumin and electron metal.

Electrical Properties.—These products have valuable electrical properties, possessing high dielectric strengths and resistivity and low power factors. As the chlorine content increases the dielectric constant diminishes.[13]

Other Properties.—These include thermoplasticity, and good water resistance.

Incorporation into alkyds increases the speed of dry.[14] The addition of chlorinated diphenyls to short oil varnishes increases adhesion and the Kauri reduction value without improving durability.[15] They give gloss to films and because of their high refractive indices impart apparent depth. A table of properties of liquid chlorinated diphenyls (AROCHLORS) is given below. The properties of solid chlorinated diphenyls are included elsewhere in the tables devoted to synthetic resin properties.

Description.	B.Pt.	S.G. (25° C.).	Flash-point (° C.) Cleveland Open Cup.	Fire-point (° C.) Cleveland Open Cup.	R.I. (20° C.).
Arochlor 1242	311°–356° C.	1·374 1·393	176–180	334 to none at b.pt.	1·627 1·629
Arochlor 1248	330°–350° C.	1·445 1·456	196	None	1·630 1·631
Arochlor 1254	352°–381° C.	1·543 1·550	None	None	1·6407 1·6410

Uses

Advantage is taken of the electrical properties of chlorinated diphenyls in the following ways. They are used as transformer oils and as dielectrics for cables and condensers.[16] A plastic, fusible, tacky insulating composition is made from a mixture of rubber and chlorinated diphenyl [17] (> 60 per cent chlorine). A blend of chlorinated diphenyl, ninety parts and wax ten parts, is used as an insulating material.[8]

Waterproofness is exploited in many kinds of water-resisting compositions. Details have been given of a spar varnish comprising chlorinated polyphenyl, tung oil and linseed stand oil.[18] A waterproof coating for regenerated cellulose sheets consists of plasticised chlorinated diphenyl with paraffin wax. A waterproof dressing for textiles contains

in addition to the chlorinated diphenyl, ceresine wax and aluminium stearate.[19] A dilute solution of a polystyrene resin in benzene plasticised with a liquid chlorinated diphenyl, is used as a waterproof seal for metal caps of containers.[20]

Anti-corrosive lacquers are based on chlorinated diphenyl and chlorinated rubber. They may be used to protect underground pipes, or duralumin from sea-water.[21]

A typical fireproofing lacquer consists of a mixture of chlorinated diphenyl and chlorinated higher boiling diaryls, with linseed and tung oils.[18] As impregnating materials for fireproofing, chlorinated diphenyls are stated to be superior to ammonium phosphate.[7, 22] When chlorinated solvents are used also, lacquers may be made which are non-inflammable both before and after application.

Other uses include adhesives such as are involved in the manufacture of splinter proof glass; as binders for cork in linoleum manufacture; with rubber, sulphur and sulphur accelerator in compositions for the protection of metal sheets in transit;[23] as a substitute for shellac in sealing waxes wherein a mixture of black chlorinated diphenyl, rosin and pigment is used;[24] with chlorinated rubber in thermoplastic moulding compositions; in composite resins with ester gum, coumarone, mixed phthalic and rosin esters,[25, 26] or alkyds; and in resins specially designed for compatibility with nitrocellulose derived from chlorinated diphenyl, ester gum and toluene sulphonamide-formaldehyde resin.[26]

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Polyamide (Nylon) Resins

These resins originated in the work of Carothers, reported extensively in the *Journal of the American Chemical Society*. The polyamides can be derived from two different types of reaction.

1. From ω-amino carboxylic acids, their lactams, or ester, chloride and anhydride derivatives.

2. From the reaction between dicarboxylic acids and diamines containing a free hydrogen atom in each amino group.

Suitable amino acids are ω-amino caproic, ω-amino pelargonic, and ω-amino undecylic acids. Pelargonolactam (10 pts), and mixed xylenols (12 pts.), are heated to 215° C. In the early stages water is eliminated as steam, but the heating is continued for an hour or so, and the xylenol finally distilled off under vacuum.

For the second type of reaction, which seems to be the more popular of the two, dicarboxylic acids such as sebacic, suberic, pimelic and adipic acids are convenient. Suitable diamines are the tetra-, penta-, hexa- and decamethylene diamines. The reaction which occurs requires approximately molecular proportions. On warming, salts are formed, and on further heating these condense in chain form. For example, hexamethylene diamine (26·4 pts.), adipic acid (33·2 pts.), and mixed xylenols (60 pts.), are heated at 218° C. for seven hours. The polyamide is recovered by pouring the product into alcohol, when it separates as a white granular precipitate.

The simple polyamides have fairly sharp melting-points usually within the range 150°–270° C., and good alkali resistance, but they are hydrolysed by mineral acids. Their specific gravities are usually just over unity: 1·04–1·08. From the varnish maker's point of view the above types of polyamides are not very suitable for general use because of their restricted compatibility. They are soluble only in rather inconvenient solvents—in phenol, cresol, formamide, acetic and certain other acids.

These polyamides in phenolic solution have, however, found an important application in high temperature coatings for copper wire. The resultant films have exceptional solvent resistance, which is far superior to that of the old oil-base wire enamels.

A very interesting development is the work conducted on the reaction between diamines and the polymeric fatty acids of drying and semi-drying oils described by Cowan, Lewis and Falkenburg.[1] Norelac is a hard resinous material produced by these means.

Approximately equivalent proportions of polymeric acids, consisting of the di- and trimeric acids derived from linolic and linolenic acids, and ethylene diamine, are heated together.

The following is an example of a resin suitable for varnishes. Polymeric acids (15·82 pts.) are heated to 150° C. in the presence of carbon dioxide, and a 70 per cent aqueous solution of diamine (2·3 pts.) is slowly

added. The temperature is then increased to 170° C. the pressure slowly reduced, and the temperature finally raised to 200° C. for a short time. The product is run out and allowed to cool to a hard resin.

Norelac, unlike nylon, is readily soluble in a large number of solvents, including chlorinated hydrocarbons, alcohols, ketones, amines and fatty acids.

Films of Norelac have good flexibility and adhesion and good resistance to water, dilute acetic acid, dilute and concentrated caustic soda, and 75 per cent sulphuric acid.

Norelac films absorb oxygen and become insoluble.

The properties which prevent the general use of resins of the Norelac type are their thermoplasticity, low melting-point, and the softness of the resultant films.

Norelac is most suitable for use in spirit varnishes to replace shellac, and in certain finishes where chemical resistance is required.

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Silicon Resins

Resinous organic products of silicon have engaged the attention of varnish makers for a good many years past, but it is only within the last year or so that definite indications have appeared that they are important intermediates with unique properties, and that they have come to stay.

Broadly, there are two types of silicon compound which are of interest. The first includes the silicon esters, and the second, the products of hydrolysis of the alkyl or aryl silicon chlorides.

Silicon esters, of which the so-called ethyl silicate has been explored the most extensively, is considered by King to be an organic solution of colloidal silica and ethyl silicate.[1] They dry rapidly in two distinct stages; gelling occurs due to evaporation of solvent, and this is then followed by a hardening process which is the result of a reaction between the ester and the moisture of the air. The hydrolysis yields alcohol, and silicic acid, which ultimately dehydrates into silica.

These silicon esters in the past have suffered from the defect of poor keeping qualities, demonstrated by a coagulation of the colloidal silica, but manufacturers now claim that the keeping properties have been considerably improved.

Lacquers or pigmented products made from silicon esters have useful fire and heat resisting properties, and they are claimed to withstand temperatures of the order of 500° C., and have been recommended also for use on porous cement, and for building stone preservation.

Additions of silicon ester to nitrocellulose lacquers greatly increase

the adhesion and elongation of the resultant films but decrease their tensile strengths.[2]

Klein and Nienburg have prepared the orthosilicates of certain fatty materials, but no information is available on their value in film-forming compositions.[3] The fatty mono- or diglycerides are heated with $Si(OEt)_4$ at 150°–160° C. The ortho silicates from α-mono-olein, α-monobutyrin and α-β-dibutyrin are all non-crystalline. α-Monostearin has a m.pt. of 70° C. and α-β-distearin a m.pt. of 68° C.

The silicon esters of the type represented by the formulæ $SiEt(OEt)_3$ or $SiBu(OEt)_3$, yield, on hydrolysis, products which are soluble in organic solvents. They provide films with good adhesion which are stated to be more resistant to heat and weather than bakelite or alkyd films.[4]

The resinous materials of silicon which have become popular lately are the products of hydrolysis of the alkyl and aryl silicon chlorides, and these have come to be known commonly as the "silicones". Suitable compounds which undergo this hydrolysis are monomethyl silicon trichloride (CH_3SiCl_3) or dimethyl silicon dichloride $(CH_3)_2SiCl_2$. The process of resinification or polymerisation as the result of hydrolysis, consists firstly in the production of hydroxy compounds, which subsequently condense together to give high molecular weight polymers. These are characterised by a Si—O—Si—O chain formation, with methyl or similar groups attached to the silicon atom.

The alkyl or aryl silicon chlorides are made by a modified Grignard process and the method of procedure has been given by Rochow and Gilliam.[5] Methyl, ethyl, or other organic magnesium bromide is reacted with silicon tetrachloride in dry ether, and the organic silicon chloride formed is hydrolysed by pouring on to ice.

The trialkyl or aryl silicon chlorides (chlorosilanes) on hydrolysis yield the corresponding silanols. These condense to simple ethers (disiloxanes) and provide the liquid silicones. The dialkyl or aryl silicon chlorides hydrolise to the bifunctional silanediols, which on condensation yield thermoplastic resins. The monoalkyl or aryl silicone chlorides hydrolise to the trifunctional silanetriols ($RSi(OH)_3$). Their condensation products are thermosetting resins of the types which are of the most use to varnish makers.

Such products have remarkable heat resisting properties, and for this reason they are exploited in high temperature resisting compositions. It is claimed that these resins resist a temperature of 200° C. for a year without perceptible change.[6] The only effect of heating at 550° C. for sixteen hours in vacuum, or at 450° C. for one hour in hydrogen, is slight discoloration.

Silicon resins are not easy to manufacture on the large scale, and for some time to come they must be recognised as one of the very expensive types of resin. They are, however, being manufactured in fair quantity.

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CHAPTER 8

SOLVENTS AND DILUENTS

THE number of solvents and diluents encountered in the varnish factory of to-day is vastly greater than it was twenty to thirty years ago. This great expansion may be attributed to the following facts. Probably the most important factor was the advent of synthetic resins. Both alkyds and phenol formaldehyde resins were responsible for the inclusion of strong aromatic solvents in varnishes or media. Although these resins possess many unrivalled properties, they have, in addition, certain defects which it is essential to eradicate. Because of the inferior flow of alkyds when brushed, special solvents have been introduced as flow inducing agents, such as Decalin, dipentene, pine oil, etc. The skinning tendency of phenolic resins with tung oil has led to the introduction of solvent dispersing agents among which may be included dipentene, butyl alcohol and butyl glycollate. Urea formaldehyde resins influenced the use of butyl alcohol. This solvent has been especially useful also in the production of stable solutions of metallic soaps. The formulation of complex synthetic compositions as media for spraying and stoving enamels, provoked an incursion into the whole range of solvents commonly used for cellulose products.

Nowadays there is no sharp line of demarcation between the maker of cellulose lacquer and the varnish manufacturer, except that normally the former does not make oleoresinous compositions by a heating process, and the latter does not make solutions of cellulose nitrate. Midway between these extremes, however, are a multitude of products which are not the monopoly either of the cellulose lacquer maker or the varnish manufacturer. These products include lacquers and media involving chlorinated rubber, rubber, vinyl resins, processed shellacs, polystyrene resins, and acrylic resins, all of which require careful selection of solvents.

Secondly, the industrial consumer of varnish products has revealed himself to be very discerning and critical. This has often necessitated the technologist to survey the whole field of organic liquids and to choose from it any which yield the desired result. Finally, the advent of the solvent type of paint removers did much to increase the normal range of solvents.

SOLVENT RECOVERY

After Application

Considerable quantities of solvents are used in the varnish trade, and once they have performed their primary function of presenting compositions in a form suitable for application as films, nothing further is required of them. They evaporate and generally become a total loss. Varnishes or media contain volatile solvents varying from 20 to

75 per cent of the whole. Often, as is the case with synthetic materials, the solvents are of an expensive type.

Solvent recovery is a difficult process and its success is dependent on many factors; the volatility of the solvents, the concentration of the vapour, the continuity of the evaporation process, the complexity of the solvent mixture, and the chemical stability of the solvents. Jordan [1] states that when the evaporation of solvents occurs in enclosed or partly enclosed spaces the question of recovery is relatively simple. Such favourable conditions occur in conveyor ovens, drying towers, and processes where large film areas are passing over hot plates, the whole of which can be covered by a hood.

The methods commonly adopted for solvent recovery are absorption or condensation. The vapours may be absorbed by high boiling liquids, or by absorbent solids such as activated alumina, charcoal and silica gel. The condensation process merely consists of cooling the vapour-air mixture often with increased pressure.

During Manufacture of the Varnish

The foregoing concerns solvent recovery after application of the film-forming composition. Other methods of effecting economy in the use of solvents are practised in the modern varnish factory. Batches of material which for some reason have become unusable are treated for recovery of solvents by subjecting the material to steam distillation. This process is particularly suitable for compositions of the lacquer type, containing relatively low boiling, water immiscible, solvents, although satisfactory results have been obtained also with medium boiling petroleum hydrocarbons. If facilities are not normally available for working off accumulated cleaning spirits used for ball mills, filter presses, etc., they may be subjected to the steam distillation process with advantage. The use of an iron still with steam is safe, even for the regeneration of solvent mixtures from nitrocellulose lacquers.[2] Merz offers the advice that the non-volatile residue in the still be removed whilst it is hot and molten, for it may solidify on cooling.[3]

Another source of appreciable loss of solvents is during the thinning process of varnishes. In the early stages a considerable amount of solvent disappears as vapour, for the normal temperature at which thinning commences is about 200° C. Such losses can be minimised, of course, by thinning at the lowest convenient temperature, but often the temperature needed is 200° C. or higher. The best type of plant for thinning consists of a large tank fitted with a close fitting lid, a mechanical stirrer and a reflux condenser. The hot oil-resin mixture is pumped into the tank and thinned in the usual way with agitation. Whilst this procedure reduces evaporation losses, precautions are necessary. Alternatively, using the same equipment, it is often possible to add the hot varnish or resin to the thinners, already in the mixer. Ebullition of the thinners is thus greatly reduced. If after thinning the varnish is allowed to stand

for several hours or overnight in the thinning tank, condensed solvent will occur, unmixed, as a separate layer at the surface of the varnish. Before pumping the varnish away or withdrawing a sample it is obvious that the whole must be agitated. Again, it happens sometimes that resins or, driers have to be heated with solvent to effect solution. This process, too, can be conducted under a reflux condenser with advantage. Occasionally, it happens that a varnish or medium is too thin for a special purpose, and the wasteful procedure of "sweating off" the excess solvent or thinner is adopted. The volatile solvents can be condensed.

Conservation by Formulation

Attempts have been made to conserve solvents in another direction. Compositions are made with the minimum amount of solvent and then sprayed hot on to surfaces. This method of application is used successfully for spraying black bituminous enamels on iron or steel, for shellac mixtures, and for nitrocellulose lacquers.[4] Such methods of application have led to modifications in the solvents used. For successful hot spraying a solvent is chosen with a convenient boiling range which does not evaporate too quickly. Slow evaporation is necessary to obtain the desired flow.

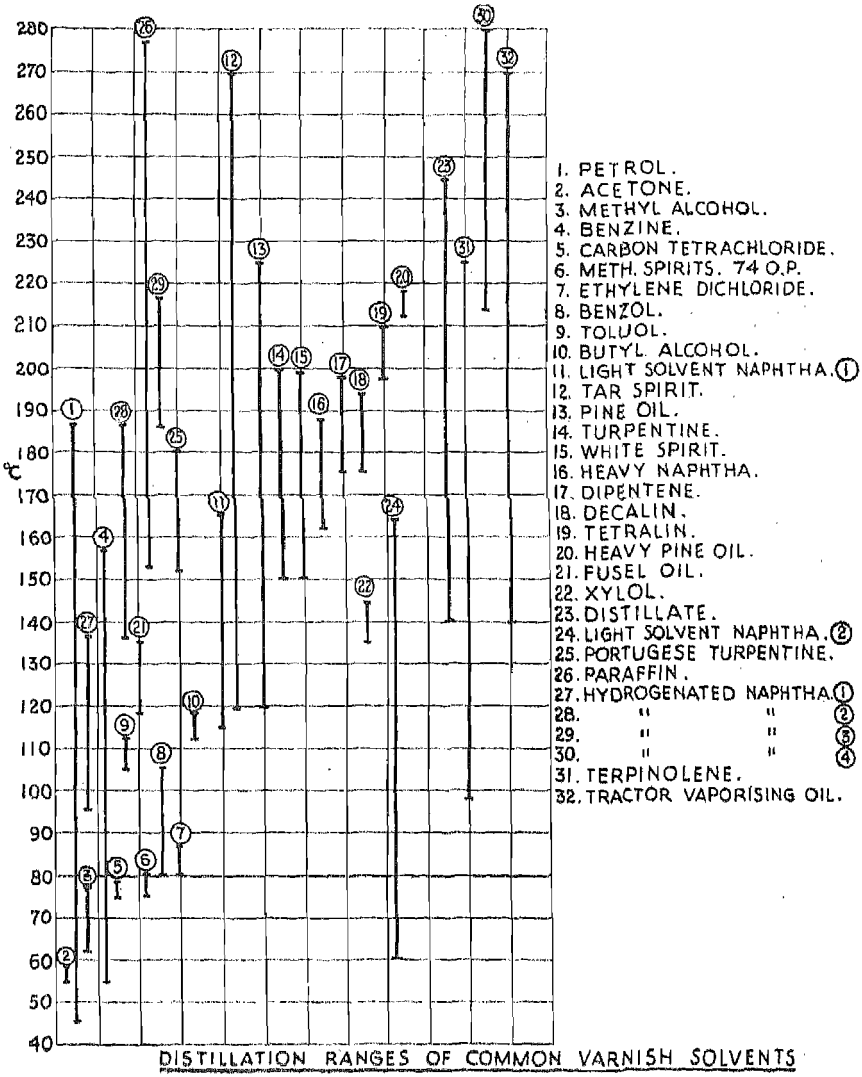
Consideration of the Properties of Solvents

Boiling Range

For convenience solvents are often subdivided into groups based on their boiling ranges, and two authorities agree on the same rough classification:[5]

Low boilers, b.p. below 100° C.
Medium boilers, b.p. 100°–150° C.
High boilers, b.p. above 150° C.

Boiling range of a solvent is an important property since it provides certain valuable information. There are but few solvents, used in varnish manufacture, which approximate to pure compounds, notable exceptions being benzene, toluene, xylene, industrial alcohol, and acetone, to quote some examples. Most solvents, even including those mentioned above, if not purified, are complex mixtures of widely differing chemical constitution, or mixtures of homologues. A boiling range determination is, therefore, a good criterion of purity. Furthermore, it provides clues pointing to the presence of low-flash constituents if low boiling fractions are found, or to the presence of non-volatile residues, if the solvent has a very extended boiling range embracing constituents with a very high boiling-point. Boiling range determinations are relatively simple to conduct, and are used frequently to provide a rough guide to evaporation rates, the determination of which are not so straightforward. It should be understood, however, that the property providing additional information on evaporation rates is the vapour pressure. It is possible to encounter liquids which possess a low boiling range, but have an evaporation rate lower than that of liquid with a higher boiling range. Further,



DISTILLATION RANGES OF COMMON VARNISH SOLVENTS

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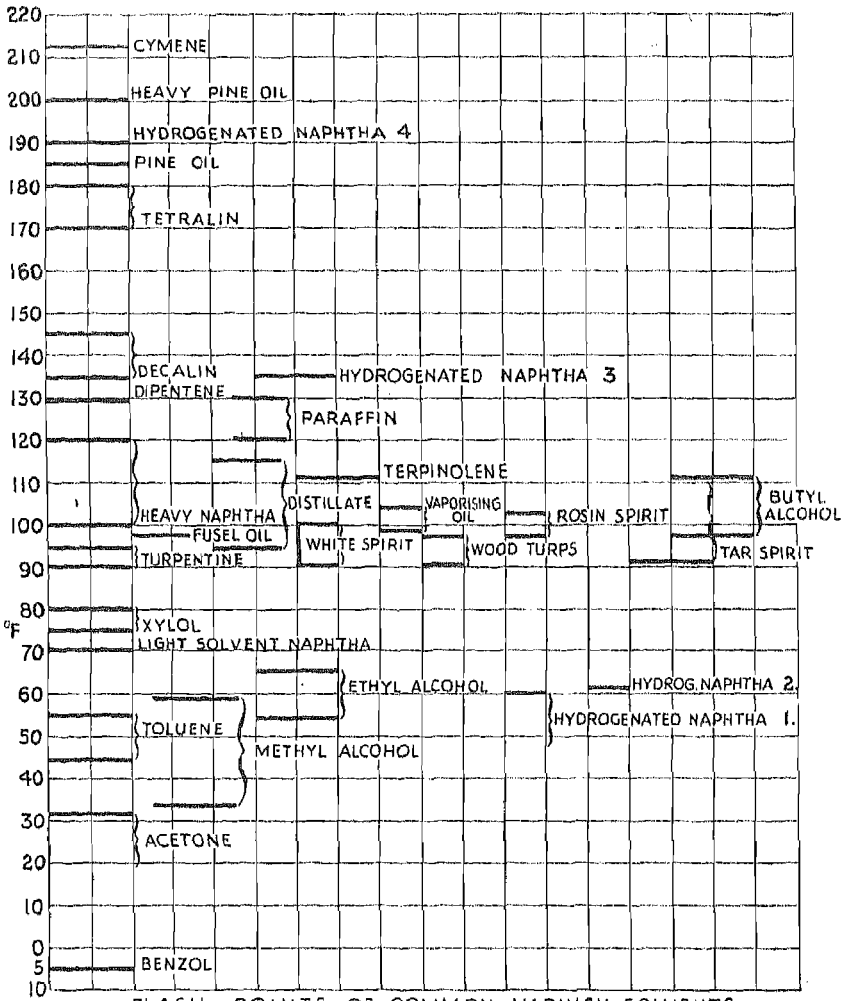

FLASH POINTS OF COMMON VARNISH SOLVENTS

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it is important to remember that boiling ranges provide information on evaporation at temperatures which are greatly in excess of those normally met with in industrial practice, and that a variable increase in vapour pressure with temperature rise may lead to erroneous deductions. A detailed account of the method commonly adopted for the determination of boiling ranges is given in B.S.S. 290.

Mixtures of solvents cause abnormalities in the temperature of boiling. Lewis, Squires and Sanders [6] state that a constant boiling solvent mixture is not generally a constant evaporating mixture at the drying temperature of the film. Bennett and Wright, however, provide other experimental evidence.[7]

Evaporation Rate

Definition of Volatility.—When is a solvent considered to be volatile ? This is a question, the answer to which is known by every varnish technologist, but which is a little difficult to formulate in precise terms. White spirit is a volatile solvent, and solvents with evaporation rates rather slower than this are still considered volatile. Paraffin, however, can hardly be classed as a volatile solvent when evaporated at room temperature. At best it is only partly volatile. It is at once obvious that volatility must be described always in relation to temperature, for at higher temperatures paraffin is completely volatile. It has been suggested elsewhere that Tetralin is the standard by which to assess volatility at normal temperatures. A solvent is considered to be volatile when its evaporation rate is equal to or better than that of Tetralin.[8]

Evaporation Rate and the Effect on Dry.—The rate of evaporation of a solvent from a film may control, to a large degree, the rate of drying of that film. A low boiling solvent with a close boiling range will evaporate rapidly and immediately permit the film to complete its normal process of drying by oxidation and/or polymerisation. A slowly evaporating solvent will retard these subsequent drying processes, and solvents containing a few per cent of practically non-volatile residue may inhibit drying indefinitely. This is demonstrated by substituting white spirit in a varnish by paraffin, or by distillate, which is a petroleum hydrocarbon intermediate in boiling range between white spirit and paraffin. Both distillate and paraffin have this small percentage of relatively non-volatile material.

Factors Influencing Evaporation Rate.—Evaporation rate is influenced by the prevailing temperature, the relative humidity, the vapour pressure, latent heat of vaporisation, conductivity, specific heat, surface tension, vapour density, solvent power and molecular weight of the solvent, the average concentration of the vapour in the air above the evaporating solvent, and the degree of association of the molecules. According to Gardner, based on experimental evidence, the evaporation rate of a solvent is proportional to the product of three constants ; the diffusion coefficient, molecular weight and vapour pressure.[9]

Varnish Constituents

In the form of a varnish film the rate of evaporation is governed by other factors, including the presence of other solvents, the nature of the oleo-resinous material or resin in solution, the viscosity and the thickness of film. The concentration of the solution influences evaporation rate. The greater the amount of solute present the more the lowering of vapour pressure. Experiments conducted by Battline on solutions of castor oil in benzol, of varying concentration, have demonstrated the lowering of vapour pressure.[10] Mayer includes other factors, such as the method of application, whether by spraying or brushing, the porosity of the undercoat, and the type and quantity of pigments present.[11]

An example of the effect of solvent mixtures on evaporation rate is the mixture of two common varnish solvents, white spirit and naphtha. When the mixture contains 85–90 per cent of white spirit and 10–15 per cent of naphtha, a definite minimum evaporation rate is obtained.[12]

Solvent Retention.—In varnishes there is no doubt that the nature of the solute and the viscosity of the film play a very important part in controlling evaporation rate, more particularly in the latter stages of the process. This phenomenon is commonly known as solvent retention. Films of shellac and nitrocellulose have been shown to retain traces of solvent weeks after the films were considered dry. Processes have, in fact, been devised to season pyroxylin sheets by removal of retained alcohol. This is accomplished by successive treatments with ethyl acetate and V.M.P. naphtha, followed by drying.[13]

Interesting facts on the subject of solvent retention have been recorded by Bogin and Wampner. They have found that when the flow of a lacquer film ceases it may still contain as much as 25 per cent of the volatiles. When the film is dry to touch as much as 13 per cent of the volatiles may still be present.[14] 5–8 per cent of the volatiles may be present after one week's air drying.

Resins, especially those of the highly polymerised types, exhibit strong solvent retention. Retention of solvent may give false impressions of the flexibility, adhesion and tensile strength of a film.

During the evaporation of mixed thinners the composition alters. This is important, and is a factor which must always be considered in formulation. Metzinger has published the results of work on this subject.[15]

Chilling and Blushing.—Rapid evaporation leads to the phenomenon of chilling or blushing. The extent to which it occurs is governed by the reduction in temperature which is consequent upon evaporation.

When a liquid evaporates it absorbs heat from its surroundings, that is, the surface with which it is in contact and the surrounding air. When the air, which always contains some water vapour, is chilled below its dew-point, moisture is deposited. If the components of the residual film have affinity for water, the deposited water will be absorbed and distributed throughout the film, until a stage is reached when one component begins to separate. This separation is the visible sign of blushing. If the residual film has no affinity for water, blushing does

not occur, for the deposited water is always kept strictly at the air-liquid interface. The more quickly a solvent evaporates the greater the extent of chilling; and the higher the humidity of the air the greater the tendency to deposit water.

To some extent water miscible solvents, like ethyl alcohol, can cope with water depositions and remove them from the film by conjoint evaporation. There is, however, a limit to the efficacy of ethyl alcohol in this respect. Butyl alcohol forms azeotropic mixtures with water and is sometimes used as a blush preventive. Butyl acetate is also claimed to be useful in removing water and minimising blushing.[16]

A method for evaluating solvent mixtures with respect to blushing tendency is described by Mindlin and Zeldovitsch.[17]

A thermometer is suspended in a thermostatically controlled air cabinet. Its bulb is coated with lacquer and the time taken for it to reach its minimum temperature is recorded. The shorter the time the greater the blushing tendency.

Determination of Evaporation Rate.—There are many methods of determining evaporation rates. The commonest method used in routine testing of raw materials merely consists in putting one or two drops of the solvent under test on a filter paper, and recording the time taken for it to evaporate. The evaporation rate may be stated either as minutes or as units, the units being based on the time taken for the evaporation of a very volatile solvent like ether. This method is sufficiently accurate to distinguish between normal and abnormal white spirits. It shows the difference between white spirit and higher boiling petroleum distillates very easily. According to Ivanovsky, however, this method may give unreliable results when used to determine evaporation rates of pigmented compositions or lacquers.[18]

Another common method of determining evaporation rate is to weigh or measure a convenient amount of solvent in a shallow basin, and allow it to evaporate under the prevailing atmospheric conditions against a standard solvent. The loss in weight is determined from time to time. This method is useful because it provides information on the amount of relatively non-volatile material present after evaporation at air temperature. This non-volatile residue is very important in air-drying compositions, since it may result in retarding the normal drying process. For stoving compositions, the presence of slowly evaporating solvent fractions may cause excessive flow or even cissing.

An improvement on this method has been used by Rubek and Dahl. Their device ensures a constant area of evaporation throughout the whole process, and consists in covering the bottom of a flat pan with a piece of filter paper which is held down securely by means of a small tripod.[19] Shank increases the area of evaporation by distributing the evaporating solvent or varnish over the surface of lead shot. Special balances have been used for determining losses rapidly and accurately, and the Hart evaporation balance is typical.[20]

A method due to Wolff and Zeidler is based on the measurement of the viscosity increase of a film consequent upon the evaporation of the solvent.[21]

A mechanically driven turntable is the basis of an Evap-O-Rotor described by Lowell.[22] The Jolly balance is used for evaporation rates at elevated temperatures.[23]

A method for determining the evaporation rate of the solvents from a varnish film, due to Gardner, consists in applying the varnish, from a weighing bottle, by means of a brush to glass panels. These are then weighed at frequent intervals and the losses determined.[24]

Other methods for the determination of evaporation rates are due to Poleich and Fritz, Hofmann, Ivanovsky,[25] Bent and Wik,[26] and Wetlaufer and Gregor.[27]

Evaporation rates as determined by different workers are liable to be very misleading because of variations in purity, method and conditions. For this reason it is considered inadvisable to include here published information, involving figures, of which much is available.

Flash-Point, Inflammability, Explosive Mixtures and Auto-Ignition Temperatures

The tendency of the vapour from a solvent to ignite is an important factor in assessing the value of a solvent for use as a varnish constituent. Not only are low-flash solvents a great risk during the manufacture of varnishes, etc., but there are many restrictions relating to the use or transport of low-flash products. Specifications for varnish compositions often stipulate that the flash-point shall not be below 90° F., in other cases not below 80° or 73° F. Thus, in evaluating a solvent its flash-point must not be overlooked. When once a solvent has been selected as suitable, subsequent deliveries should be checked carefully, especially if the solvent is delivered in tank waggon. With white spirit, for example, there have been cases in the Author's experience where abnormally low flash-points have been detected. This was traced to the fact that the tank had been used for transporting petrol previously, and had been drained incompletely before refilling.

Formulæ enabling flash-points to be predicted have been suggested. Ormandy and Craven have suggested two such formulæ, one based on the relation between flash-point and initial boiling-point, and the other based on the relation between flash-point and pressure.

$$\text{F.pt.} = 0{\cdot}736 \times \text{initial boiling-point} - 72^\circ \text{ C.}$$

This is satisfactory for hydrocarbons.

$$\text{F.pt.} = x \log p + y$$

where x and y are constants and p is the pressure.

In the case of petroleum solvents, Harrap and Evans[194] draw attention to the fairly close relation between the volatility, measured

by the 50 per cent distillation temperature, and the flash-point as determined by the Abel Flash Point Apparatus. This contention is shown in the table below :

Solvent	Flash-pt. (°F.)	Temperature at which 50 per cent is distilled (°C.)
S.B.P. 1	−52	67
S.B.P. 2	−40	74·5
S.B.P. 5	− 7	93
S.B.P. 3	+15	105·5
Rubber Solvent (R.S.)	+40	121
S.B.P. 6	+74	145·5
White Spirit	+93	163

It should be noted, however, that the relationship only holds for petroleum fractions of close boiling range.

Adjustment of Flash-point.—It happens frequently during formulation that it is necessary to raise the flash-point of the solvents used. There are several methods of doing this. The most obvious one is to delete or replace the solvent with the lowest flash-point. It is a common error to assume that the addition of high flashing solvent, of necessity results in an increase of flash-point. Often the reverse is the case for the flash-point may be reduced. Thus solvents prone to form azeotropic mixtures are avoided. A good example of lowering of flash-point is given by Cannegieter. Varnish naphtha (flash-point 35° C.) when mixed with solvent naphtha (flash-point 39° C.) to give a concentration of solvent naphtha of 10–25 per cent shows a flash-point of 24° C.[28] Another method of raising the flash-point is to incorporate some very volatile chlorinated hydrocarbons. It has been recorded elsewhere that the possibility of the recurrence of inflammability may arise, due to the selective evaporation, from the mixtures of the chlorinated hydrocarbons. Selective evaporation may be prevented by using solvents with similar vapour pressures.[29]

Measurement.—Flash-points are measured by means of the Abel, Abel-Pensky, or Pensky-Martens instruments. Rossmann and Haug have recorded the necessity for stirring during flash-point determinations. Errors are especially noticeable with viscous materials, for when these were unstirred the flash-points were as much as 1·8° too high. It is suggested, therefore, that the Pensky-Martens apparatus with stirrer is used.[30]

It is not always convenient to use the standard method for flash-point determinations since a good deal of time is required, and the verdict of the laboratory on a consignment of solvent may be required urgently. In these circumstances, rough determinations may be made by warming the solvent slowly in a small metal crucible, stirring continuously with a thermometer, and passing a lighted taper across the surface of the warm

solvent. The results obtained are always higher than those from a closed apparatus, but the method is accurate enough to detect solvents which are very abnormal.

Inflammability.—Inflammability is governed by the concentration of the vapour and its combustibility, which in turn is governed by chemical constitution. Further, the vapour concentration controls the violence of the explosion upon ignition. The lower explosive limit corresponds with the flash-point. Each solvent has, in addition, an upper explosive limit. Beyond this the concentration of vapour is too great to support combustion.

Auto-Ignition Temperatures.—Since most varnishes are thinned at very elevated temperatures the auto-ignition temperature of the solvent is worthy of consideration. Generally, the auto-ignition temperatures of most solvents are much higher than the normal varnish process temperatures. Figures given by Thompson, however, show that turpentine has an auto-ignition temperature of 252°–262° C. and gasoline about 267° C.[31] These temperatures are well within the limit used in varnish manufacture, and careless thinning may result in a fire, even if the thinning takes place in the absence of a flame. The auto-ignition temperature varies with the type of surface of the containing vessel.

Solvent Power

Of all the properties to be considered in the evaluation of solvents, solvent power is undoubtedly one of the most fundamental. Many methods have been suggested for its determination, but mostly they have the defect of artificiality and are rather too remote from the precise conditions of practical use. Wherever possible it is recommended that the solvent be examined for solvent power, for the solutes with which it will be used in the varnish factory. This procedure receives the criticism that with common solvents, like white spirit, which are used for a great variety of purposes, the process of evaluation becomes unduly prolonged in the effort to cover all possibilities. This has led to the introduction of short cuts, which, as indicated already, do not always duplicate manufacturing conditions.

In assessing solvent power several factors have to be considered.

1. The chemical structure of the solvent. Chemical structure plays an important part in conferring solvent power.

2. The speed with which solution is effected. The shorter the time necessary the better the solvent.

3. The viscosity of the final solution. Usually the lower the viscosity of the solution the greater the solvent power.

4. The stability of the solution. On standing some solutions tend to deposit insoluble matter. Often a good solvent will delay or prevent this.

5. The minimum possible concentration of solute in solvent which is obtainable. On diluting solutions excessively with solvent, precipitation

sometimes occurs. The greater the permissible dilution without separation the better the solvent power of the solvent.

6. The tolerance of the solvent for non-solvents. The greater the amount of non-solvent which can be added to a solution of solute in the solvent, the better the solvent power of the solvent. This is an important point if the solvent is expensive and can be cheapened by addition of diluent.

7. The solvent may form part only of a solvent mixture. Many mixtures form extremely powerful solvents, even more powerful than any of the individual solvents.

8. The temperature necessary to effect solution, and the sensitivity of the resulting solution to temperature fluctuations. Reduction in temperature may cause precipitation.

Effect of Chemical Structure.—The influence of chemical structure on the solvent power of a solvent will now be considered. The molecules of some solvents exhibit a potential difference across themselves and are known as polar solvents. They are recognised also by possessing high dielectric constants. All solvents containing oxygen, for example, in hydroxyl groups, etc., are polar. Such oxygen containing solvents *include water, ketones, esters, ethers and alcohols.*

Alcohols are very polar, esters and ketones are less polar than the alcohols, and ethers have only slight polar properties. Non-polar solvents are represented by aliphatic and aromatic hydrocarbons. Unlike the ordinary hydrocarbons chlorinated hydrocarbons have slight polar properties. Polar solvents are most effective with polar solutes, and non-polar solvents with non-polar solutes. Of the commoner varnish ingredients the following have been given as polar; alkyd and phenol formaldehyde resins,[32] shellac and cellulose esters. Non-polar ingredients include rosin modified phenolformaldehyde resins, coumarone, drying oils, bitumens, some waxes and rubber.

Ostwald has provided useful means of predicting solvent power based on a consideration of dipole moments (μ) and dielectric constants (ϵ). For cellulose acetate the function μ^2/ϵ is small for inactive liquids, increases for liquids which demonstrate swelling action, and is greatest for liquids which are true solvents.[33]

Aromatic Content.—Other differences in chemical structure affect solvent power. With most varnish compositions and resins, aromatic hydrocarbons are much better solvents than aliphatic hydrocarbons. It has been recorded that for resins, aromatic hydrocarbons have twice the solvent power of naphthenes and four times that of paraffins.[34] The superiority of aromatic hydrocarbons has led, therefore, to the suggestion that hydrocarbon solvents should be assessed for solvent power on results derived from analyses for aromatic content. Extraction of aromatic content by oleum has been used. Another method of obtaining the percentage content of aromatic and unsaturated aliphatic olefinic hydrocarbons is by the dimethyl sulphate test. Equal volumes of dimethyl

sulphate and solvent are gently shaken together. On standing, the amount of solvent absorbed by the dimethyl sulphate is determined. The percentage solubility is the dimethyl sulphate value.[35]

Velocity of Solution.—Velocity of solution is an important guide in assessing solvent power, and furthermore it may exert a profound influence on production. This may be examined quite easily by weighing out equal amounts of solute, and by dissolving them in similar amounts of solvents, by cold churning for a specified convenient time. The solvents used being, in one case, the solvent for assessment and in the other the standard solvent. At the end of the allotted churning time the amount of insoluble matter is determined.

For lacquer type compositions a method for determining velocity of solution has been suggested by Wolff, Zeidler and Toeldte.[36] Drops of the solvents under test are placed simultaneously on the dried film, and after a convenient time the effect on the film, as evidenced by swelling or dissolution, is examined. Solutes which yield strong continuous unsupported films lend themselves to the following methods of determining the velocity of solution. The method of Kraus consists in suspending strips of the films in the solvents, and noting the time necessary for the part of the film in contact with the solvent to detach itself.[37] Bare and Nelson support a film on a wooden frame and place on it a weighted pad soaked in the solvent. The time taken for the pad to completely penetrate the film is taken.[38]

Another aspect of the velocity of dissolution of dried films is in the application of lacquers and varnishes over undercoatings. If the solvent of the finishing material possesses a high velocity of dissolution for the dried undercoat film, many defects may arise. In bad cases the undercoat will be dissolved, badly swollen, or may be detached from the surface. In less severe cases it may be softened slightly, and this will result in application difficulties if brush application is used, as evidenced by "pulling" and imperfections in flow, in difficulty in "joining up" and in loss of gloss due to absorption. Stewart and Berwick have conducted experiments on the effect of thinners in overlapping varnish films.[39]

Viscosity of Solution. Viscosity of solution is another means of assessing solvent power. It is commonly held that the lower the viscosity of a solution the greater the solvent power of the solvent. For nitrocellulose, for example, McBain, Harvey and Smith, have stated that the viscosity of solution is proportional to solvent power.[40] With alkyds, too, the relationship between viscosity and solvent power is accepted. Medium oil length alkyds are not generally readily soluble in white spirit or petroleum hydrocarbons, in that a limit of diluent is soon reached at which the solution becomes turbid. Furthermore, the rate of reduction of viscosity consequent upon additions of such solvents is low. Often there is no apparent viscosity change for quite large additions. With solvents of better solvent power, like that possessed by the aromatic hydrocarbons, the rate of viscosity reduction is more pronounced, and

additions of solvent produce a steady continuous reduction in viscosity. Thus, the solvent power of solvents may be determined by dissolving a constant amount of solute in similar amounts of various solvents, and determining the viscosities of the resultant solutions. Alternatively, constant amounts of solute may be dissolved, and solvent added until the viscosities of the solutions are equivalent to that of the solution from the standard solvent. Solvent power is then judged from the amount of solvent required to attain "constant viscosity."

In using viscosity determinations as a guide to solvent power, the influence of traces of impurity may be very marked. In illustration of this, a small percentage of butyl alcohol often causes very substantial viscosity reduction. Traces of water also exert pronounced effects.[41]

Experiments conducted by Kolke, on linseed stand oil and tung oil stand oil, with various solvents, showed variations in viscosity. The solution of lowest viscosity was obtained with solvent naphtha, then turpentine, petroleum and Decalin.[42]

Kurtz, Harvey and Lipkin use a viscosity method for assessing the solvent power of mineral spirits for resins. The resin is dissolved in a

TABLE SHOWING THE SOLUBILITY OF ALKYDS IN DIFFERENT SOLVENTS

		Amount of Solvent required for Alkyd Resin. (Vis. 2-5 poises at 25° C.).	
		Alkyd resin 1 (100 pts.).	Alkyd resin 2 (100 pts.).
	Per cent.		
1. Turpentine White spirit Decalin	33 33 34	115	130
2. Turpentine Naphtha	75 25	105	115
3. White spirit Naphtha	75 25	95	110
4. White spirit Naphtha Butyl alcohol	67 22 11	70	85
5. White spirit Naphtha Cellosolve	67 22 11	76	90
6. White spirit		100	122
7. Turpentine		115	132
8. Decalin		115	132
9. Hydrogenated naphtha		90	108

standard mixed solvent consisting of aliphatic, aromatic and naphthenic compounds. A solution of similar concentration is prepared, using the

solvent under test, and the ratio of the two viscosities obtained is called the "resin solvency."[43] A similar method has been used in which the solute is similar to the substances with which the solvent will be used in practice, i.e. the viscosities of hydrocarbon solvent solutions of a mixture of boiled linseed oil and phenolic resin (3 : 1) have been compared.[44]

Solvent.	Viscosity of Solvent (poises) A.	Viscosity of Solution (poises) B.	Ratio B/A.
Petroleum ether	0·004	0·28	70
Benzol	0·006	0·45	75
Sangajol	0·010	0·73	73
Carbon tetrachloride	0·010	0·73	73
Turpentine	0·016	1·15	72
Decalin	0·019	1·30	69
Tetralin	0·022	1·60	73

Based on experiments with stand oils, conducted by Wolff and Toeldte, it was concluded that low viscosity of solution is not, necessarily, indicative of good solvent power. Boller has obtained some interesting results with stand oils and has shown that when thinned equal parts by volume the viscosity of the resultant solution is governed by the initial viscosity of the solvent.[45] (See Table above.)

Doolittle emphasises that viscosity determinations alone are insufficient to make a true evaluation of solvent power. Viscosities and dilution values correlated by phase diagrams give more reliable information.[46]

Stability of Solution.—Stability of solution on standing, and resistance to precipitation on excessive dilution are co-related. Solutions of synthetic resins, in particular, should be kept under observation for several days before making a decision on the suitability of the solvent, for sometimes the solution may become cloudy or separate into two layers.

Concentration of Solution. Dilution.—The importance of examining solvents for the maximum permissible dilution of varnish compositions with them, is readily appreciated. Consumers frequently thin compositions to accommodate their own peculiar application methods, and this sometimes necessitates relatively large additions of diluent. Where the maker of the varnish composition also supplies the thinner, he should ensure that the thinner will permit adequate dilution without risk of precipitation, if complaints are to be avoided.

Some methods for determining solvent power are based on the degree of dilution possible with a given solvent. Frandsen adds similar amounts of varnish base to a number of tubes. To these tubes are added varying amounts of solvent and the contents are thoroughly mixed. After standing, the contents of the tubes are examined for precipitation. A new set of tests is then made covering the range of solvent between the first tube showing precipitation and the first one free from it. By this means an accurate estimate of the amount of solvent just causing precipitation

is obtained. The greater the amount of solvent which can be added without precipitation the higher the solvent power of the solvent. For this type of test Gardner suggests the use of a short oil varnish base comprising 100 lb. synthetic resin and 12 gallons of oil. Alternatively, a heavy blown oil can be used in place of the varnish base.

Kauri Butanol Test.—The well-known Kauri butanol test is really a dilution test. It consists, essentially, in titrating a given volume of a Kauri solution in butanol with the solvent under examination, the end-point being, when the opalescence caused by precipitation of gum is sufficient to cause blurring of normal print. The greater the amount of solvent which can be added before precipitation occurs the better its solvent power. Care is needed in preparing the Kauri solution. The Kauri is selected specially and cleaned, and 100 gm. are dissolved by refluxing in 500 gm. butanol (b.p. 114·4°–116·6° C.). After standing, the clear solution is decanted. Precautions must be taken to obtain consistency of results by this method. Beard, Shipp and Spelhouse have provided the following information. Temperature of titration influences results appreciably, higher temperatures yielding higher apparent solvent power. Other factors influencing the result are the concentration and amount of solution, the presence of water and the quality of the Kauri used.[48] Any variation in Kauri from different batches can be shown by titrating with a standard grade of mineral spirits, kept expressly for this purpose. Many criticisms have been levelled against the Kauri butanol test for solvent power, the chief of which is its artificiality, for it shows very little similarity to the conditions under which the solvent will be used in practice. Moreover, it is hard to conceive how one such test can provide information on a solvent, which may be expected to accommodate all sorts of products. A relationship between the viscosity of a phenolic varnish and the Kauri butanol value has been found.[49]

A modification of the Kauri butanol test, due to Gardner, more nearly approaches conditions encountered in practice. A run Kauri solution in turpentine is titrated with petroleum spirit until cloudiness develops. The Kauri solution comprises "run Kauri" (25 per cent running loss), dissolved by warming in an equal volume of turpentine (b.p. 153°–170° C.). A further improvement is claimed by titrating with solvent, a mixture of equal volumes of the above Kauri solution and a heavy bodied oil.[50]

Aniline Point.—Aniline point determinations are sometimes used to evaluate solvent power. For mineral spirits aniline point and Kauri butanol value have been found to be in agreement.[49] The aniline point is the maximum temperature at which a mixture of equal volumes of aniline and solvent become immiscible. Thus the lower the aniline point the better the solvent. The details of the method are as follows: 3 c.c. of fresh aniline are mixed with 2·5 c.c. solvent in a tube and warmed. On cooling, the temperature is recorded when cloudiness develops. A

check on the end-point is made by making further slight additions of solvent and repeating the above procedure.[35] Reeves claims that the aniline point test for mineral spirits is superior to the Kauri butanol test, on the grounds of easier reproducibility, and freedom from the necessity of standardisation.[51]

Mixed Solvents.—As has been indicated already, the tolerance of solvents for non-solvents is important. White spirit may be regarded often, either as a poor solvent or merely as a diluent. It is about the cheapest of varnish thinners, and for this reason its addition to varnish compositions is important, economically. It is frequently used in conjunction with the more expensive solvents such as turpentine, and the aromatic solvents. Thus both the white spirit and these solvents should be checked carefully for solvent power, for the higher the individual solvent powers, the larger the percentage of white spirit permissible in the solvent mixture, and consequently the cheaper it will be.

Where mixed solvents are essential to obtain the desired result, the solvent power of the constituent solvents should not be determined individually, but only in admixture with all other constituents. Many solvent mixtures exhibit exceptionally high solvent powers, and permit varnishes to be made which otherwise would have abnormally high volatile contents.

The effect of additions of butyl alcohol or Cellosolve, to mixtures of white spirit and naphtha, for use with alkyds, has been shown already in a previous table. Bogin has confirmed this fact.[52] Single solvents do not always yield clear solutions. Thus damar in benzine is opalescent. If, however, mixed solvents are used, clear solutions are claimed. Mixtures of benzine and diacetone alcohol (95 : 5), or benzine and alcohol (90 : 10) are suggested. Mixed solvents for polyvinyl acetate resins are methyl alcohol (38 pts.) with benzene (62 pts.); or ethyl alcohol (100 pts.) with benzene (135 pts.) and water (13 pts.). Cellulose acetate is insoluble in the dimethylether of ethylene glycol. Addition of water, however, to the glycol, yields a satisfactory solvent.[53] A mixture of ether and alcohol dissolves cellulose nitrate, which is insoluble in either of the individual components. When dichlorobutane is mixed with ethyl alcohol, or with ethyl alcohol and toluol it dissolves both cellulose nitrate and acetate.[54]

Varnishes based on hard phenolic resin and tung oil, when thinned with white spirit or turpentine, may be opalescent or may develop opalescence on ageing. This can be prevented by the addition of a few per cent of Cellosolve. Mixed solvents are used also to effect other improvements such as easier spraying and better adhesion. Additions of white spirit and other petroleum hydrocarbons, or turpentine, to spirit varnishes is a common procedure. When petroleum hydrocarbons are used in conjunction with industrial alcohol, each hydrocarbon should be carefully tested for miscibility since variation in behaviour is possible.[55]

When mixed solvents are used, especially if one component has poor solvent power only, their evaporation rates and the factors influencing

them must be studied carefully. If a relatively non-volatile inferior solvent is left behind, precipitation may occur in the film during drying.

Temperature.—Temperature controls solvent power to a marked degree. Generally, solvent power increases with increase of temperature. In testing the suitability of a solvent for a given solute, it is advisable to subject the final solution to lower temperatures than those normally encountered, and to examine for separation. A few exceptions are known where better solvent power is obtained by reducing the temperature. The solvent power of an alcohol-ether mixture for cellulose nitrate increases with reduction of temperature. At — 50° C., methyl alcohol becomes a solvent for cellulose esters.[56]

Liquefied butane, propane, sulphur dioxide, sulphuretted hydrogen and ammonia are solvents for both natural and synthetic resins.[57]

Solvent Power and Surface Tension.—Papkov has suggested surface tension determinations as a means of evaluating solvent power. Aromatic solvents with surface tensions greater than 37 dynes per cm. dissolve or swell acetyl cellulose. If the surface tension is less than 37 dynes per cm. the solvents do not dissolve it. For aliphatic solvents the critical limits of surface tension for solubility are 21·7–29·3 dynes per cm. Outside these limits aliphatic solvents have no action on acetyl cellulose.[58]

Stability

Solvents vary considerably in their stability. Fortunately, the most widely used solvent, white spirit, is an inert material and can be stored under any conditions without change. This, however, is not the case with turpentine. Due to its unsaturation, turpentine readily undergoes oxidation. Peroxide formation, and the properties of oxidised turpentine, are discussed elsewhere. Turpentine is not normally transported in metal drums. Wooden barrels are commonly used, although Spoon has stated that for turpentine from the Dutch East Indies sheet iron drums are satisfactory.[59] Corrosion around the bronze cocks of turpentine storage tanks is evidenced by a green coloration. Smith and Holman have conducted experiments with the object of preventing the deterioration of turpentine during storage. A difference in effect was noticed in using containers of different metals. After two years, in a steel container coated with shellac, no great changes were observed except in rate of evaporation. In a galvanised iron drum similarly coated, a larger amount of sticky residue was produced in the turpentine. Among agents which are satisfactory for the prevention of deterioration are acid sodium sulphite, calcium oxide, powdered magnesium, pyrogallol and hydroquinone. With the last two, however, some darkening occurs. In the opinion of these two workers, deterioration can be prevented by adding the above agents, keeping the containers full, withdrawing water as rapidly as it accumulates and coating the containers with shellac lacquer.[60] Alcoholic shellac solution, pigmented

with red lead, and plasticised with venice turpentine, is another composition which is stated to prevent interaction between turpentine and the metal of the storage containers.

Like turpentine, dipentene also oxidises in the presence of air although to a lesser degree. Hydroterpin and balsam turpentine are not perceptibly auto-oxidisable.[61]

Decalin is completely saturated and stable, but Tetralin tends to oxidise, as shown by darkening in colour and the formation of resinous substances.

Some esters may hydrolyse under moist conditions. Since hydrolysis gives rise to free acid which may have a detrimental effect upon the varnish composition, especially if pigmented, this tendency must be considered. Experiments conducted by Kummel on lactates are interesting in this connection. When ethyl lactate is boiled with 10 per cent of water only 0·05 per cent of free lactic acid is eliminated. No appreciable free acid is obtained when butyl and amyl lactates are boiled with 10 or 20 per cent of water.[62]

Ethyl ether forms explosive peroxides. Di-isopropyl ether is particularly dangerous.[63]

The chlorinated hydrocarbons, as a group, probably show greater instability than any other group of solvents. Trichlorethylene attacks metals, including aluminium, tin, copper, lead, brass, and soft steel, when heated, a reaction assisted by the presence of water.[64] Carbon tetrachloride attacks lead and copper. The presence of alcohol stimulates corrosion.[65]

Storage tanks coated with bakelite or cellulose lacquers can be made resistant to the attack of carbon tetrachloride.[66] Certain substances are said to inhibit corrosion and among them are hexylresorcinol, butyl mercaptan and triethylamine. Phenols are also used to prevent the decomposition of chlorinated ethanes.[67]

The deterioration of chlorinated hydrocarbons generally, on storage, is reduced by adding liquid paraffin, aliphatic petroleum hydrocarbons (b.p. 40°–232° C.), azo dyes and amino compounds.[68]

In its corrosive action on metals, dichlorobutane is intermediate between dichloroethane and trichlorethylene, the latter having the greatest corrosive action.[69]

At ordinary temperatures in the absence of light and moisture, methylene chloride is stable.

Odour

The odours of the vapours of solvents, used for varnishes and lacquers, deserve more consideration than is usually given to them. In formulation it is as well to eliminate or mask solvents which possess strong penetrating unpleasant smells, for they may form the basis of complaint subsequently. Female operators have been found by experience to be particularly sensitive to unpleasant odours, and their

complaints have necessitated the eradication of an otherwise satisfactory finish.

Most good white spirits do not possess objectionable smells, although the vapours from inferior grades have been described as sickly. The smell of turpentine is accepted as pleasant, possibly because of its rich balsam tang, and small additions to bad white spirits act effectively as deodorants. Other deodorants, apart from proprietary brands which are used, are dipentene, solvenol, oil of cloves, oil of lemon grass, oil of lavender, oil of sassafras, pine oil, nitrobenzene, vanillin, and sometimes traces of guaiacol.

Benzol has a particularly pungent smell, and should be avoided whenever possible for this reason alone. None of the smells of aromatic hydrocarbons is pleasant, but toluol and xylol are preferable to the naphthas. Even small percentages of naphtha in white spirit mixtures are very apparent.

Tar spirit has a very penetrating smell which is decidedly unpleasant. The dislike for it is accentuated because of its pronounced tendency to cling to clothes, etc. Its use is restricted to a few special high temperature bituminous enamels.

Butyl alcohol is often regarded as objectionable, possibly not so much for its smell, as for the peculiar irritating effect it has on the throat, inducing coughing. The betrayal of its presence by this means is practically infallible.

The somewhat objectionable characteristic smells of cyclohexyl derivatives probably accounts for their limited popularity.

Gardner has devised a method for comparing the odours of drying films. It consists, essentially, of coating the inside of a gallon container with the film under test. The container is so constructed that it possesses a number of holes at the side of the container near the bottom and a larger hole in the cover.[70]

Colour

Solvents normally do not possess any marked colour. When they are not water white, the colours are pale only, and would not be regarded as objectionable for most purposes. Where lacquers of exceptional paleness are required a discoloured solvent should be avoided. Whilst the colouring matter may have no effect upon the resultant film, but this, however, is not always the case, its effect on the initial colour of the lacquer or varnish may prompt a potential customer to reject it for this reason. It is not an uncommon experience for the first impression of a lacquer on a customer, to assume a strong influence in deciding in favour of a particular product. Solvents which are most likely to be discoloured are coal-tar naphthas. Solvent naphthas often possess a strong golden-yellow colour, a characteristic property which is governed by storage conditions. Special naphthas free from this defect are available.

Varnish Constituents

Tar spirits vary considerably in colour from almost water white to a deep reddish-brown, depending upon the extent of purification. Since its chief use is as a powerful solvent for high temperature stoving bituminous enamels, colour is unimportant. For other purposes it would, of course, have to be taken into consideration.

Old turpentine stored under adverse conditions may develop a pale greenish or pale yellow colour. Fusel oil, which is a crude mixture of several different alcohols, sometimes has a pale yellow colour.

In testing solvents for colour they should be examined simultaneously for clarity. Contamination with water produces turbidity, and this is a fairly common condition of wood turpentine and freshly distilled coal-tar naphthas. Whilst it is not advisable to use wet solvents, little trouble will be experienced under most circumstances, and in any case ageing for a short time clears up the turbidity.

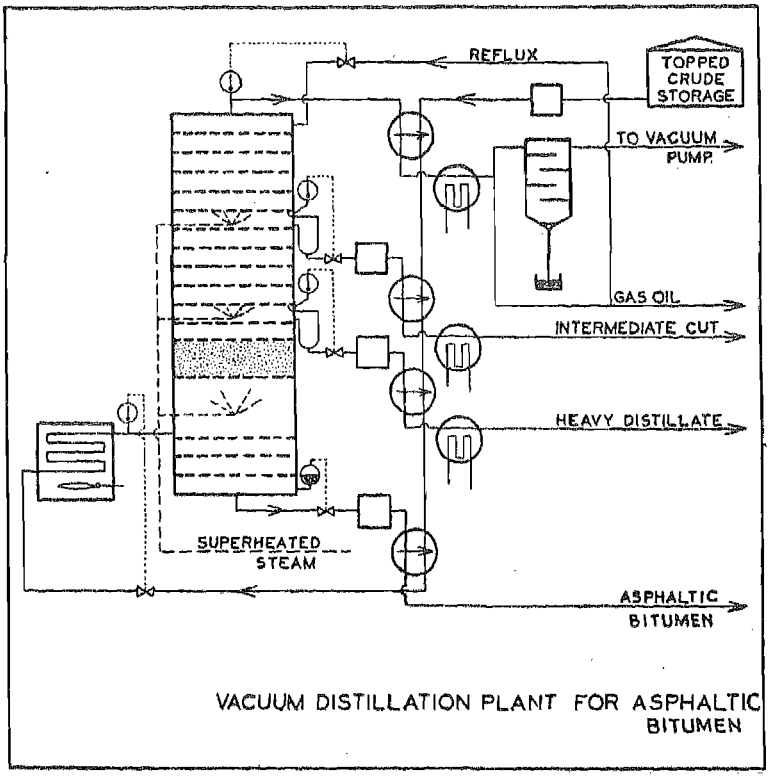
Impurities

The impurities most likely to be present in petroleum hydrocarbons are sulphur compounds. Tests for presence of these objectionable bodies are carried out by placing a bright piece of copper strip in the flask during boiling range determinations. In the absence of sulphur compounds the copper remains untarnished. According to Upson this test is not specific for sulphur compounds in petroleum hydrocarbons, because the sulphur may be present in many different molecular forms and a negative result may be obtained. For petroleum thinners, however, containing sulphur reactive in paints, the copper strip test is satisfactory.[71]

Up to ½ per cent of thiophene may be present in coal-tar benzene, and commercial toluol and xylol may contain thiotolene and thioxene respectively. These sulphur compounds contribute to the objectionable smells of these aromatic hydrocarbons. The presence of thiophene in benzol is easily detected by shaking benzol with a solution of isatin in concentrated sulphuric acid. If thiophene is present a deep blue colour develops. Mercaptans in hydrocarbons are determined by a method due to Malisoff and Anding.[72]

Water may be regarded as an impurity in solvents, especially in solvents whose affinity for it is great. Water in hydrocarbon type solvents is estimated by Dean and Stark's method which consists in distilling the solvent mixed with pure toluene. The water is carried over with the distillate. Using the same principle Holley recommends using a mixed solvent consisting of amyl acetate (5 vols.) and amyl valerianate (1 vol.), because he claims that it gives more accurate results than the toluene distillation method. As in this method, water is carried over with the distillate.[73]

Large amounts of water in water miscible solvents are easily detected by means of specific gravity. With alcohol an increase is observed. A saistfactory method of quantitative estimation of water in alcohol is due to Schutz and Klauditz.[74] The alcohol is heated for two hours under



VACUUM DISTILLATION PLANT FOR ASPHALTIC BITUMEN

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reflux with 10–15 per cent of dry calcium carbide. The acetylene is passed into acetone, and the solution is then added to Ilosvay's cuprous chloride reagent, whereby precipitation of cuprous acetylide is caused. The acetylide is dissolved in 10 per cent acidic ferric sulphate. The resultant ferrous sulphate is titrated in the normal way with N/10 potassium permanganate (1 c.c. of N/10 $KMnO_4$ is equivalent to 0·0018 gm. water).

Toxicity

In evaluating a solvent for use in a composition which may have widespread industrial application, its physiological effects are of great importance. The subject of toxicity of solvents has received considerable attention in the last few years.

Solvents may find their way into the human body by several routes. The commonest way is by inhalation. They may be absorbed also directly through the skin or may be taken accidentally through the mouth. When solvents are in constant contact with the skin they may dissolve out from it the fats, and skin diseases may be caused.

In varnish manufacture there are many processes where the operative is liable to be exposed to solvent vapours. These occur during thinning of hot varnish or resin mixes, where in the initial stages large amounts of vapour are evolved. Solvents which are commonly used for hot thinning include petroleum and aromatic hydrocarbons, turpentine and tar spirit. The latter is especially objectionable because of the pronounced irritant effect it has on the eyes. Another operation where high concentrations of vapour accumulate is during the centrifuging of hot varnishes. This treatment stimulates excessive frothing and releases large volumes of vapour. Where large quantities of varnish are being continually filtered, or where large quantities of volatile thinners like benzine or industrial alcohol are added to mixers, high vapour concentrations may be set up. Another essential part of varnish manufacture is the cleaning of storage tanks and making pots. In the former, men frequently have to get inside, whilst in the cleansing of making pots the operator works with his head inside at least part of the time. There is little risk of absorption of solvent by means of the mouth except by pure accident. The only chance of poisoning by this means, is if the operators leave their food exposed to atmospheres where high concentrations of vapour exist almost permanently. Articles of food like bread and biscuits have been known to absorb vapours of xylol to such a marked degree that they have become quite unpalatable. There is, therefore, some slight risk that solvents with less penetrating tastes may be assimilated in food undetected.

Other operations in varnish manufacture involve almost constant contact with solvents themselves. This condition occurs in cleaning containers, tanks, pots and other plant by means of solvents. Furthermore, some workmen develop the habit of cleaning their hands with solvent,

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In the application of varnish compositions where large areas are coated in enclosed spaces, such as in the coating of silk, calendered cloth, paper, etc., the atmosphere is likely to become heavily charged with vapour. Spraying facilitates the rapid formation of high vapour concentrations more than any other method of application. This occurs because the composition is ejected into the air in the form of a very fine mist, and the conditions are very favourable for rapid volatilisation.

Damage to workpeople by the toxic action of solvents can be minimised and often eliminated entirely by taking certain elementary precautions. Obviously the use of the more toxic solvents should be avoided altogether, or if their presence is essential the amount used should be kept to a minimum. The most important precaution which should be adopted is the installation of an adequate ventilation system. The presence of a strong smell may be taken sometimes as a rough indication of harmful vapour concentration, but it is unwise to rely solely upon this evidence. In high concentrations some vapours have such powerful smells that it is quite impossible to remain in the contaminated atmosphere for more than a short time. On the other hand, the sense of smell is often dulled by other vapours, and even strong concentrations may remain undetected until other symptoms appear. To illustrate the fallacy of relying entirely on the sense of smell, mustard gas vapours are known to possess the power of dulling the normal sense of smell, and in this example the results would be disastrous if its presence were undetected. The vapour concentration in the atmosphere can be kept to a minimum by avoiding the use of low boiling highly volatile solvents whenever possible, and since volatility increases with temperature, the temperature of the workroom should be kept low also. It may not be practical to provide adequate ventilation in every section of the factory, and in this circumstance operatives should be provided with respirators. When it is necessary to clean large storage tanks by introducing a man inside them it is not sufficient to supply the man with a respirator only. The vapours, because of their high density, displace air, and there may be insufficient air remaining to support breathing. The only safe way to proceed with tank cleaning is to use a respirator, the intake of which is fastened to a long air supply line led away to a clean air supply. The risks run by allowing workmen to store their food in vapour-laden atmospheres have been emphasised already. Absorption of solvents through the skin can be minimised by the use of hand preparations which are well rubbed in before work is commenced. These preparations also have the advantage in that they facilitate the cleaning of the hands subsequently, and obviate the constant use of strong solvents for this purpose.

The toxicities of the commoner varnish solvents will now be considered. The order chosen is that of importance of the solvent to the industry rather than of the degree of toxicity.

Petroleum or Aliphatic Hydrocarbons

White Spirit.—It is fortunate that although these hydrocarbons are the most widely used they are the least toxic. Cases of poisoning by white spirit vapours are rare. A record states that the symptoms produced include giddiness and vomiting. An extreme case of intoxication resulted in unconsciousness. The chief trouble promoted by white spirit is dermatitis, and it is observed when operatives are in contact with the liquid for long periods. Some have a distinct susceptibility to develop skin disease in contact with white spirit, and cases have been noticed where only one workman, out of several doing precisely similar work, has suffered. His removal from the influence of the solvent effected a cure, but his re-introduction to it for a short period only reproduced the original symptoms. The parts affected were the arms and hands, although inflammation of the eyes occurred also, which may be attributed to the action of vapour.

Other Petroleum Distillates.—Hayhurst advises against the exposure of workmen for long periods to skin wetting by petroleum distillates.[76] Pfanner reports that paraffin causes dermatitis also.[77] Engelhardt confirms the tendency of petroleum spirit to cause hyperæsthesia of the skin.[78] Petrol taken internally causes intoxication and narcosis. Pneumonia also seems to accompany these conditions.[79] Inhalation of petrol vapour in several cases has resulted in the following conditions : unconsciousness, vomiting, convulsions, delirium, weak respiration, and contraction of pupils. In less severe cases the symptoms are those normally associated with alcoholic intoxication, or if the vapours have been inhaled over long periods of time the patient exhibits lassitude, head noises and even unconsciousness ultimately. The author can testify to the effect of exposure to low boiling petroleum hydrocarbons. Exposure of about an hour's duration caused definite intoxication, a blurred vision, inabilty to think clearly and general unsteadiness. A peculiar feature was that for several days afterwards a smell like that of cyclohexyl derivatives was detected at each inhalation.

The composition of petroleum products varies considerably, and the records of cases of poisoning have not always taken this factor into account. Lazarev, from experiments conducted on mice, has arrived at the following conclusions. The toxicity of benzine is mainly due to the presence of cycloparaffins. Specific gravity sometimes serves as a guide to toxicity, which increases with specific gravity. Lifschitz states that the toxicity of benzine vapour increases with temperature up to 24° C.[81] Like white spirit, petrol may also cause eczema.[82]

By comparison with benzol, a petroleum distillate with a similar evaporation rate has only about half the toxicity.[82]

Aromatic Hydrocarbons

In this group are included the naphthas, xylol, turpentine, toluol, benzol, Decalin, dipentene and Tetralin. It contains some of the most toxic of all solvents.

Benzol.—Benzol, toluol and xylol damage the central nervous system.[83] Ferguson, Harvey and Hamilton, from experiments on rabbits and rats, have shown that benzol is more toxic than toluol, but that its effects disappear more rapidly. Its greater toxicity is attributed to its greater evaporation rate. The initial indications of benzol poisoning may be a stimulation. Toxic effects are secondary.[84] Milburn has also considered the relative toxicity of benzol, toluol and xylol.[85] Benzol is highly toxic. Recent work on the toxicity of benzol has been conducted by Charlier and Angenot.[86] The symptoms it produces in cases of acute poisoning vary from nausea, vomiting, headache, giddiness and tightness in the chest to convulsions, paralysis and unconsciousness in more severe cases.[87] The symptoms of chronic benzol poisoning are, according to Smith, headache, excessive fatigue, dizziness, nausea, anorexia, nervousness, numbness and tingling. More severe cases of chronic benzol poisoning exhibited hæmorrhages from the gums and nose, and eruptions.[88] The symptoms of benzol poisoning are similar to those characteristic of acute scurvy.[89] Death may result from severe cases of poisoning. With aromatic hydrocarbons in general the tendency to promote dermatitis is always present.[77] Hamilton records that sufferers from benzol poisoning also show diminished resistance to infection.[90] Nervousness and lung troubles are reported to be characteristic of females suffering from benzol poisoning. Hansen has reported fatal cases where pulmonary lesions were indicated. He draws also a distinction between the effects of light and heavy doses of benzol vapour. The former produce temporary headache and nausea, but heavy doses may cause unconsciousness and cyanosis. The heart and breathing may be affected also.

Because of the toxicity of benzol, its estimation in the air has attracted a good deal of attention. Suggested methods are given below. A method due to Harbeck and Lunge, later modified by Smyth, consists in nitrating the benzol vapour by passing it into a mixture of nitric and sulphuric acids. The dinitrobenzene formed is removed and titrated with titanous chloride. In another method, benzol vapour is collected on the surface of glass beads at the temperature of solid carbon dioxide. After purification it is shaken with 5 c.c. of ferrous sulphate ($\frac{1}{2}$ per cent. solution) and 2 c.c. of hydrogen peroxide (1 per cent.). If 0·005 c.c. of benzol are present a brown colour is produced in five minutes. If more benzol is present a black precipitate is obtained. A method involving direct quantitative estimation consists in absorbing the vapour on activated charcoal and determining the increase in weight. Another method of benzol estimation consists in drawing the air containing the vapour through concentrated sulphuric acid containing a few drops of formalin. The reddish-brown coloration, produced in the presence of benzol, is compared colorimetrically with a standard solution of sodium nitroprusside.[92]

Toluol.—Toluol, like benzol, has a strong narcotic effect, but unlike the latter it does not produce convulsive neurotoxic effects.[93] Although it is normally stated to be less toxic than benzol, toluol in high concentra-

tions may be more toxic. In fact, Lehmann states that under these conditions it is two-thirds more toxic than benzol.[94] According to Stocké, the symptoms of acute poisoning are intoxication, headache, nausea, disturbance of equilibrium, vomiting, paræsthesia and unconsciousness, although the later state is rarely produced.[95] With chronic poisoning, in addition to headache, nausea and vomiting, other symptoms are sleeplessness, giddiness, incapacity to work, nervous irritability, loss of appetite and throat irritation. Workers suffering from chronic toluol poisoning exhibited, in addition to other symptoms, digestion troubles and hypersensitivity to alcohol.[96] A fatal accident during the application of a chlorinated rubber paint was attributed to toluol poisoning.[97]

Xylol.—Xylol is considered to be less toxic than benzol. The symptoms it produces are very similar to those of toluol poisoning. Up to 1937 no fatal case had been reported. A spectrographic method of estimating xylol has been devised by Luszak.[98]

Coal-tar Naphthas.—From a consideration of the chemical composition of coal-tar naphthas, it would be expected that their toxicity would resemble that of the purified fractions, benzol, toluol and xylol.

The effect of naphthas is likely to be variable, because of the great variation in composition and volatility of commercial grades. Normally toxicity is not so marked as that of benzol. In general its acute effects are similar to those of benzol, although bronchial irritation has been reported in addition. Cases of chronic poisoning are few, but again the symptoms are similar to those of benzol, toluol and xylol.

Recent work on the toxicity of coal-tar naphthas has been reported by Bowditch and Elkins, and Taylor.[99] According to Twort and Twort gas-tar products may cause dermatitis and cancer.[100]

Turpentine.—Turpentine has attracted a good deal of attention in the past by reason of its supposed toxic properties. Controversy has occurred, in attributing the poisoning to turpentine, or to the lead pigments which so often have been associated with it. There is no doubt, however, that turpentine has definite toxic effects. Taken by the mouth it is an irritant poison, causing both irritation of the stomach and the kidneys. Inhalation of the vapours has produced fatal results. Symptoms of acute poisoning are intoxication, irritation of mucous membranes, headache, giddiness, nausea, sickness, stomach pains and possible kidney injury. Cases of chronic turpentine poisoning are rare. Normally cases of poisoning recover fairly rapidly. There is evidence of turpentine attacking the skin. Engelhardt has stated that it can cause hyperæsthesia of the skin.[78] With reference to the tendency of East India turpentine to cause dermatitis or eczema, Spoon claims that the effect is not general but arises through individual hypersensitivity.[101]

Dipentene.—Although dipentene is similar to turpentine chemically, up to 1937 no cases of poisoning had been reported.

Decalin and Tetralin.—The hydrogenated naphthalenes, Decalin and Tetralin, are used to some extent in varnish manufacture, but of the two

Decalin is by far the more popular. Although Tetralin has a lower evaporation rate than Decalin it appears to be far more toxic. As far as can be ascertained no cases of poisoning have been reported with Decalin. Tetralin, however, produces nervous depression and local irritation. According to Koelsch the symptoms consequent upon inhalation are not serious, including irritation of the eyes and throat, headache, sickness and nausea.[102]

Alcohols

Ethyl Alcohol.—The next most important group of varnish solvents is that embracing the alcohols. Of these ethyl alcohol, in the form of industrial alcohol, is the most widely used, followed by butyl alcohol which is next in importance. Other alcohols, such as propyl, amyl and methyl, are used to a lesser extent. The relative toxicities of the alcohols vary considerably. Apart from the fact that methyl alcohol is considered more dangerous than ethyl alcohol, the toxicity tends to increase with molecular weight. Amyl alcohol is stated to be very toxic.[103] It is confirmed that methyl alcohol is worse than ethyl alcohol, from the point of view of chronic poisoning, but ethyl alcohol produces more acute effects.[104] Exposure to ethyl alcohol vapour may produce headache, irritation of the eyes and nose, and drowsiness. Loewy confirms these symptoms produced as the result of repeated exposure to the vapour.[105] James reports that intoxication may occur through absorption by the skin.[106] Cirrhosis of the liver, and heart trouble, may be the result of inhalation of alcohol vapours. In assessing the toxic effect of alcohol the possible presence of pyridine should not be overlooked. The toxic effects of pyridine may be erroneously attributed to ethyl alcohol. Operatives who are more or less constantly in an atmosphere containing ethyl alcohol vapour do not appear to be easily affected by it. They seem to be less susceptible to its influence than others who are unaccustomed to it. Atmospheres charged with enough vapour to cause the first symptoms of intoxication in most people, have no effect on operatives who are continually subjected to the influence of the vapours. Haggard and Greenberg estimate ethyl alcohol vapour in air by decomposing it with iodine pentoxide.[107]

Butyl Alcohol.—With butyl alcohol cases of industrial poisoning are rare. There appears to be little real evidence available on the toxicity of butanol where complications, due to the presence of other solvents, are absent. This alcohol appears to cause eye irritation and anæmia. It has an immediate effect on the throat causing coughing, and exposure to the vapour produces headache.

Methyl Alcohol.—Methyl alcohol has a much worse reputation. Ingestion or inhalation may result in blindness. Where methyl alcohol has been used in enclosed spaces unconsciousness and fatalities have occurred. Further, it should be treated with great care, because it is not rapidly eliminated from the body, and thus has a cumulative effect when exposure is continuous. Like ethyl alcohol it is absorbed through skin. Other damage to the body by this alcohol includes anæmia, eye lesions and

presiratory inflammation. According to Browning,[108] the more general symptoms are intoxication, headache, vertigo, impairment of vision and gastro-intestinal disturbances. Kruger reports the appearance of eye diseases, resulting from using a varnish based on a solvent mixture, comprising methyl alcohol, butyl acetate and butyl alcohol.[109] Allyl alcohol is very toxic, and the toxicity of methyl alcohol derived from wood distillation is said to be produced by the allyl alcohol content. Allyl alcohol is absent in synthetic methyl alcohol.[110]

Propyl Alcohol.—About the toxicity of *n*-propyl alcohol, little information is available, and industrially it is not generally regarded as a dangerous solvent. It differs from ethyl alcohol in that it shows a much reduced tendency to be absorbed through the skin.

Amyl Alcohol.—With amyl alcohol and fusel oil, which is a complex mixture of several alcohols, evidence of industrial toxicity is inconclusive. According to Flury and Zernik the symptoms of chronic poisoning are, among others, headache, giddiness, vomiting, diarrhœa, irritation of mucous membranes, impairment of vision and delirium. Sometimes death occurs.[111]

Ketones

The most important of the ketones used in the varnish trade are acetone and methyl ethyl ketone. Durrans states that the narcotic action of acetone is more rapid than that of methyl alcohol. The latter, however, is much more toxic.[112]

Sklianskaya, Urieva and Mashbitz, in comparing the relative toxicities of the two solvents, record that although methyl alcohol is more toxic at low concentrations, acetone is more toxic at higher concentrations.[113]

Acetone can be drunk in small doses, apparently without ill effect, whilst exposure to vapours causes headache, irritation of the nose and throat, and intoxication. Methyl ethyl ketone irritates the eyes, nose and throat.

Chlorinated Hydrocarbons

Except in the preparation of non-inflammable paint removers, in cleaning or degreasing plant, and when used in small quantities to raise the flash-points of low flash mixtures, chlorinated hydrocarbons find little application in the varnish factory. These solvents are characterised by their strong narcotic effect. Some of them are very toxic and their use industrially has been prohibited in some cases. They should be used with great care. The order of toxicity of some of the commoner chlorinated hydrocarbons has been given as : least toxic, perchlorethylene and carbon tetrachloride, followed by perchlorethane, trichlorethylene, dichlorethylene, chloroform, pentachlorethane, and tetrachlorethane.[114] Chloroform may produce unconsciousness and death. Methylene dichloride causes irritation of the nose and throat, stimulates the action of the heart, and disorganises the respiratory system. Its narcotic effect is less

than that of chloroform. Wohlers states that it is relatively non-toxic and is used in varnishes, lacquers and removers.[115] Carbon tetrachloride causes intoxication. Sufferers from chronic poisoning show tiredness, headache, dizziness, paræsthesia, decreased potency, stomach disorders, and muscle twitching.[116] Jaundice, impairment of vision, and kidney and liver injury, are other characteristics of severe carbon tetrachloride poisoning. Tetrachlorethane is especially dangerous. Its narcotic effect is much more pronounced than that of chloroform. Jaundice and damage to the liver result from chronic poisoning. Pentachlorethane resembles tetrachlorethane in its toxicity. Trichlorethylene is a powerful narcotic but does not appear to affect the kidneys and liver. Roholm reports that it has a special intoxicating effect on certain brain nerves. Christiansen states that it may cause lung injuries.[117] Barrett, Cunningham and Johnston have conducted recent work on the toxicity of chlorinated hydrocarbons.[118]

Cellosolve

The toxicity of Cellosolve appears to be of a very low order. Apart from possible eye irritation, and probable slight damage to the liver, no other harmful effects have been discovered. Continuous exposure to low concentrations of the monomethyl ether of ethylene glycol is said to cause poisoning, however.[119]

Esters

Esters generally, of the acetate type, do not possess the toxicity exhibited by some of the former solvents.

Methyl acetate has an irritant effect on the eyes, nose and throat, but no definite cases of severe poisoning have been reported. Since on hydrolysis methyl alcohol is eliminated, the toxic effect of the ester may be due chiefly to the products of hydrolysis.

Ethyl acetate is a stronger narcotic than methyl acetate, but is similar in producing local irritation. It possesses also a tendency to cause eczema.

The evidence of toxicity of butyl acetate is generally inconclusive. Symptoms of poisoning attributed to it, are local irritation, headache, stomach disorders and bronchial catarrh.

Amyl acetate is more toxic than acetates of lower molecular weight. It is effective both as an irritant and a narcotic. It may damage the liver and kidneys, stomach and respiratory organs. Its irritant effect is further shown by its action on the eyes, nose and throat. Other symptoms of amyl acetate poisoning are intoxication, giddiness, and disorganised breathing and pulse.

Other Solvents

There are many other solvents used in varnish and lacquer manufacture in small quantities, and information on their toxicity, as well as more detailed information on the solvents already considered, is provided in a comprehensive summary by Browning.[120]

Detection and Estimation

Aromatic Content.—The estimation of aromatic content in aromatic thinners like naphtha, in petroleum hydrocarbons, or in mixtures of coal-tar solvents and petroleum hydrocarbons is important, for it is on this that the solvent power depends to a very large extent. Methods of extraction of aromatics, involving oleum and dimethyl sulphate have been mentioned already. For solvents containing small amounts of aromatics only, absorption by silica gel is suggested.[121] A method due to Grosse and Wackher is based on specific dispersions. The aromatic content is equivalent to

$$\frac{100(\delta_m - 0{\cdot}16 \times \text{Br value} - 99)}{(\delta_a - 99)}$$

where δ_m is the specific dispersion at 20° C. of the mixed solvent, and δ_a is the specific dispersion of an aromatic solvent of similar boiling-point.[122] Refractive index determinations form the basis of another method of analysis. Fuming sulphuric acid (20–30 per cent of sulphur trioxide) is allowed to react upon mixed thinners for ten minutes. The composition of the thinners is determined by a comparison of the refractive indices of raffinate and original thinner.[123] Benzol can be detected colorimetrically by its reaction with hydrogen peroxide and ferrous sulphate. A black precipitate or brown colour is obtained.[124]

Turpentine.—Turpentine polymerises on treatment with sulphuric acid, and this forms the basis of a test for purity of turpentine and for estimating the amount of turpentine in white spirit mixtures. In the turpentine polymerisation test,[125] a few c.c. of the solvent to be tested are treated with a large excess of concentrated sulphuric acid. The polymerisable portion of the solvent disappears with the acid portion, whilst the unpolymerisable part of the turpentine, together with white spirit, etc., separate as an upper portion. Turpentine itself has about 10 per cent of unpolymerisable material, and this must be considered in determining the turpentine content of mixtures. Ladd and Roberts report that thinners free from turpentine may yield 15–20 per cent of polymerisable material.[126] Qualitative tests for turpentine involve the formation of coloured bodies. When 2–3 c.c. of chloroform, and one drop of antimony pentachloride, are added to two drops of solvent, an immediate dark red colour is obtained in the presence of turpentine. The colour subsequently changes to purple and the mixture becomes turbid. A pale brown colour, changing to pink, is given by petroleum hydrocarbons and benzene. Shestakov uses tin tetrachloride which with turpentine forms a brownish oil. Further colour changes are observed when this oil is shaken with water, the colour passing successively from brown to blue, green and ultimately yellow. If a solution of turpentine in benzene is used, a brick-red precipitate is deposited.[127] Because turpentine is unsaturated a high iodine value may indicate its presence.

Esters.—Information on esters is derived from saponification values. A complete process for the analysis of lacquer solvents has been worked out by Watts and Metzinger. Methods of analysis of solvents have been described also by Martin.[128]

Alcohols.—An excellent method for estimating hydroxyl value involves the use of acetyl chloride and pyridine. Acetyl chloride solution (10 c c.; of acetyl chloride 118 c.c., diluted to 1,000 c.c. with toluene) is cooled in ice, and pyridine (2 c.c.) is added. The solvent under test is weighed into the mixture in a flask, in amount such that a substantial excess of acetyl chloride is present. The whole is then thoroughly shaken and maintained at 60° C. for twenty minutes, diluted, and shaken with distilled water (25 c.c.), and titrated with sodium hydroxide solution, using phenol phthalein as indicator. The decrease of acidity computed against the titration of a blank experiment is a direct measure of the hydroxyl content of the mixture.[129]

Secondary alcohols can be oxidised to ketones, and this procedure has been suggested for their determination in the presence of primary alcohols.

Christensen and Fulmer have devised a scheme for determining the constituents of an acetone, ethyl alcohol and *n*-butyl alcohol mixture. The alcohols are oxidised with dichromate and extracted with carbon tetrachloride. The acetone is determined by an iodometric method.[130]

A method involving Magdala red is used to distinguish between hydrocarbons or ethers, basic compounds, and hydroxy or ketonic compounds. Hydroxy or ketonic solvents give fluorescent solutions, basic solvents give solutions with no fluorescence, and hydrocarbons or ethers do not dissolve the coloured body.[131] Aldehydes obtained by the oxidation of *n*-propyl, *n*-butyl, isobutyl or amyl alcohols, yield characteristic colours after treatment with *o*-nitrobenzaldehyde under alkaline conditions.[132]

Traces of primary alcohols or similar aldehydes may be estimated by titration with 0·1*N* chromic acid in dilute nitric acid.[133]

The interaction of *o*-nitrobenzaldehyde and acetone to form indigotin has been used as a method for acetone detection.[134]

Ketones.—Ethyl alcohol or solvents which have a methyl group attached to a carbonyl group, for example, aldehydes and ketones, give a positive iodoform test. Some other alcohols, on oxidation, yield suitable ketones or aldehydes, and thus the iodoform test can be used as a means of detecting them also.

Trichlorethylene.—Trichlorethylene may be detected by the red colour obtained by treatment with pyridine and caustic soda.[135]

PROPERTIES

Petroleum Hydrocarbons

Crude petroleum occurs in many widely separated parts of the world, including Mexico, Texas, Pennsylvania, California, Southern Russia (Baku), Rumania, Galicia, South Persia, Venezuela, Burma, Assam and

Borneo. Except for the very volatile constituents, every fraction of crude petroleum has some use in varnish manufacture.

The chemical composition of crude petroleum varies considerably with its origin. Thus American crude oil, generally, is mainly paraffinic in character. Petroleum from South-Western America is claimed to be rich in aromatics.[136] Texas crude is on an asphaltum base. Borneo crude contains aromatic hydrocarbons, and benzene and toluene have been reported to be present. A white spirit with excellent solvent properties, derived from Borneo crude oil, has been sold under the name of Sangajol. Durrans states that white spirit from Rumanian crude has the greatest general solvent power.[137] Naphthenes or polymethylene hydrocarbons are characteristic of Russian oil. Petroleum from Burma contains large quantities of wax. Aromatic hydrocarbons are extracted from petroleum by means of the Edeleanus process which involves the use of liquid sulphur dioxide. Glacial acetic acid has been suggested as a selective solvent for the removal of unsaturated hydrocarbons from petroleum distillates.[138]

Fraction.	B.Pt. (° C.).	Uses.
Petrol (gasoline)	45°–185° C.	Impregnating insulating varnishes, quick setting adhesives and other quick setting products.
Petroleum ethers	1. 40°–60° C. 2. 60°–80° C. 3. 80°–100° C.	As for petrol, but for products where more rapid evaporation is required. This is possible because of absence of high boiling material.
Petroleum benzine	55°–155° C.	
White spirit	150°–200° C.	For air-drying and stoving compositions of many types.
Distillate	140°–245° C.	A cheaper solvent than white spirit, occasionally used in air-drying compositions where speed of dry is not essential. Chiefly used in stoving compositions.
Paraffin	150°–280° C.	As a thinner for stoving compositions, and as a cleaning liquid.
Lubricating oil, white oil	—	In stoving compositions to provide "slip." In paint removers.
Vaseline	—	
Paraffin wax	—	
Petroleum bitumen	—	In Brunswick blacks, black insulating varnishes, black japans, stains, etc.
Naphthenic acids	—	In naphthenate driers.

White Spirit.—The development of white spirit production and testing has been summarised by Stewart.[139]

Evidence supporting the statement of the variable composition of commercial white spirit is shown by substantial variation in specific gravity, of which the limits of 0·777 to 0·800 at 15° C. have been recorded.

Differences in solvent power are exhibited also. Variations in boiling range and evaporation rate are not so common (see table on page 284).

For many years turpentine held pride of place as a varnish thinner, but it is now retained only to exploit its characteristic smell which, alas, is still regarded by some as the true criterion of varnish quality, or in a few products to specification, or by reason of its good solvent power for certain resins. In ordinary oleoresinous varnishes, and in many synthetic varnishes, white spirit is a cheaper satisfactory substitute. Turpentine has a rather better evaporation rate than white spirit, but in the normal air-drying varnish which requires several hours to dry, the difference is unimportant. Where solvent power is of primary importance there is a logical reason for using turpentine in place of white spirit. The solubility of medium oil length alkyds in white spirit is not entirely satisfactory, for although it may be possible to thin them with white spirit, the amount of thinner necessary to obtain a convenient viscosity may be abnormally large, resulting in poor film thickness. Thus turpentine is used in the preparation of many air-drying alkyd finishes. For a similar reason, turpentine is used in place of white spirit in some pure phenolic or modified phenolic varnishes.

TABLE SHOWING THE PROPERTIES OF WHITE SPIRIT TYPE SOLVENTS TO AMERICAN, GERMAN AND BRITISH SPECIFICATIONS

	American	American	German	British
Description	Petroleum spirits (mineral spirits)	Stoddard solvent	Paint benzine	White spirit..*
Specification	A.S.T.M. D. 235–39	A.S.T.M. D. 484–40	No. 848	B.S.S. 245 (1936)
Non-volatile residue	—	—	$<0{\cdot}2$ g. from evaporation of 100 c.c.	$<0{\cdot}2\%$ at 100° C. $<0{\cdot}5\%$ at 60° F.
Sulphur compounds	No marked blackening of copper after 30 mins. at boiling-point of spirit	Only slight discoloration of copper after 3 hours at 212° F.	Free from sulphur compounds which would darken pigments	Free from objectionable sulphur compounds.
Flash-point	>100° F.	>100° F.	>70° F.	>78° F.
Boiling range	At least 50% at 176° C. 210° C. max.	At least 50% at 176° C. At least 90% at 190° C. 210° C. max.	$\not>5\%$ at 135° C. At least 90% at 200° C. At least 97% at 220° C.	$\not>10\%$ at 150° C. At least 80% below 190° C.

* Abstracted by permission from British Standard Specification 245, White Spirit, official copies of which can be obtained from the British Standards Institution, 28 Victoria St., London, S.W.1.

Other arguments extended in favour of turpentine against white spirit, are the improvements which it is claimed to give in drying time, film thickness, durability and adhesion. A good deal has been written concerning the influence of turpentine upon the normal oxidation process of unsaturated oils, wherein it performs the rôle of an intermediary in passing on the atmospheric oxygen. If any substantial advantage in drying time is obtained, which in the experience of many is very doubtful, the great discrepancy in cost between turpentine and white spirit renders preference for the former most unlikely. With reference to increased film thickness, it is true that turpentine contains a small percentage of non-volatile material which would contribute to this, but the advantage gained is practically negligible. Colledge has reported that destructively distilled wood turpentine increases the durability of paint films.[140] Dupont, by reason of the extra durability obtained for paint films by using old turpentine, records that it is more economical than white spirit even in cheap paint products.[141] Brock, however, contends that the ultimate durability is similar whether turpentine or white spirit is used.[142] The higher solvent power of turpentine tends to soften recently applied undercoatings, and enables finishing coats to key better. Wolff and Zeidler,[143] and Gardner, have emphasised the advantage of turpentine in this respect, although under some conditions softening may be a disadvantage. Advantages of white spirit over turpentine include chemical inertness, which makes for stability on storage, constancy of colour, and less tendency to lift undercoatings. Absence of smell is also considered an advantage sometimes. White spirit is less toxic than turpentine.

White spirit is a good solvent for drying oils both natural and polymerised, although its solvent power is not good enough to permit the preparation of dilute solutions of blown linseed oil without turbidity or gelation on storage. It is not a solvent for hard fats like tristearin. It is a solvent for run natural copals in sufficiently concentrated solutions, and dissolves rosin, rosin ester, copal ester, limed rosin, damar, the softer modified phenolic or maleic resins, coumarone, and long oil alkyds readily. It does not dissolve soft Manila, sandarac, shellac, accroides, hard modified phenolic resins, pure phenolic resins, hard maleic resins, short oil alkyds, urea formaldehyde, vinyl, acrylic, or polystyrene resins. It is a solvent for petroleum bitumens and gilsonite asphaltum.

Apart from its use as an oil or synthetic varnish thinner, white spirit is used in terebines and wood preservatives, as a solvent for metallic drying salts, in insecticides, in metal and wax polishes, in cleaning solutions, and in spirit varnishes based on industrial alcohol to improve spraying properties. Addition of a few per cent of white spirit to an alcoholic solution of solvent-extracted shellac (hard lac resin) is said to confer extra hardness on the dried film. A quickly evaporating petroleum distillate (b.p. 45°–100° C.) is used in a spraying lacquer containing shellac with a little accroides, dissolved in industrial alcohol.

Petroleum Ethers, Benzine and Petrol.—The lower boiling fractions from petroleum which include the so-called petroleum ethers, benzine, and petrol, are used chiefly in impregnating insulating varnishes. They are chosen for this purpose because their high rate of evaporation facilitates their removal from the internal interstices of coils, etc. They have similar solvent properties to white spirit, but specific gravity and flash-point are both substantially lower.

Petroleum Substitutes for Benzol, Toluol, and Xylol.—Aliphatic hydrocarbons from petroleum have been produced with boiling ranges similar to those of benzol, toluol and xylol, and for certain purposes substitution of these aromatic solvents has been effected.[144] The petroleum used for their manufacture must be carefully selected otherwise the solvent powers compare very unfavourably with those of the coal-tar aromatic hydrocarbons. Borneo crude rich in aromatics is chosen. The benzol substitute has a boiling range of 75°–95° C.; toluol substitute 100°–120° C. and xylol substitute 140°–160° C.[145]

Distillate.—Distillate is a petroleum fraction with properties intermediate between those of white spirit and paraffin. It is used primarily because it is cheaper than white spirit. It is used in some cheap air-drying products, but the presence of a large amount of slow evaporating material seriously retards the normal drying process. In stoving varnishes it is quite satisfactory, and its slow evaporation rate aids in stimulating good flow. In compositions where penetration is required, as in stoving impregnating varnishes for paper, distillate is a popular solvent.

Paraffin.—Paraffin has too low an evaporation rate to be used in air-drying compositions, and in many low temperature stoving varnishes or media it is also considered to be unsatisfactory. Its chief use is in high temperature stoving finishes, especially in stoving black enamels on an asphaltum base. The normal stoving temperature of these finishes is included in the range 350°–475° F. The flow of enamels on cycle frames passing through a conveyor is of the greatest importance. Paraffin enables adequate flow to be obtained, so that the possibility of accumulations of enamel with consequent rivelling is precluded. The film is kept "open" by the paraffin and any excess drains away. Paraffin is used also as a solvent for metallic soaps in wood preservatives. A characteristic of many paraffins is that they exhibit a slight bluish fluorescence in bulk.

Vaporising Oil.—Another useful petroleum hydrocarbon solvent is vaporising oil or vaporising spirit, often described by the letters T.V.O. It has a boiling range approximately intermediate between that of distillate and paraffin. It is not used for air-drying compositions because of its low evaporation rate, but is a useful solvent for stoving finishes. It is a better solvent than either paraffin or distillate because of the presence of aromatics, which may constitute up to 40–50 per cent of the solvent. For synthetic stoving finishes where a solvent of moderately good solvent power is required, such as those based on pure phenolic-resin

tung oil combinations, the use of vaporising oil is recommended. Its penetrating properties are excellent, and for this reason it is incorporated in impregnating varnishes for paper and fabric. Consignments of this solvent sometimes have pale straw colours, but for most purposes this is not considered detrimental.

S.B.P. Spirits.—S.B.P. spirits, or special boiling-point spirits to give them their full description, are a valuable series of solvents produced as the direct result of the war. They are all light petroleum solvents produced by distillation from specially selected and refined naphthas. Chemical treatment is applied to remove undesirable sulphur compounds and eliminate objectionable smell.

Before the war the varnish trade bought a large variety of petroleum solvents masquerading under many names—benzine, 770 spirit, etc. These have now been telescoped into six S.B.P.s, Pool Rubber Solvent (R.S.), Pool White Spirit, and Pool distillate.

An excellent paper by Harrap and Evans [194] gives, in exceptionally elaborate detail, the physical properties of these solvents. These two workers have done an invaluable service to varnish formulators, in that, for the first time, they are equipped with comprehensive information on the whole range of available petroleum solvents.

The whole of the information included on these solvents has been extracted from the above paper. The usual physical constants are included in the table of Constants of Solvents.

The table given below shows that the S.B.P.'s, R.S., pool white spirit, kerosene and vaporising oil consist chiefly of paraffins and naphthenes. The amount of unsaturated hydrocarbons is low, with a maximum of 2·5 per cent, but the aromatic content assumes importan proportions in some of the S.B.P.'s and the other solvents. In vaporising oil about one-fifth of the total weight of the solvent is aromatic hydrocarbon, with two-fifths naphthenes. The aromatic hydrocarbons present in these solvents may be benzene, toluene, ethyl benzene, and xylenes.

HYDROCARBON COMPOSITION OF PETROLEUM SOVENTS

(Per cent Weight)

	S.B.P. 1	S.B.P. 2	S.B.P. 3	S.B.P. 4	S.B.P. 5	S.B.P. 6	Rubber Solvent	White Spirit	Kerosene	Vap. Oil
Aromatics .	3·0	4·5	10·5	5·0	4·5	17·5	12·0	19·0	11·0	21·0
Naphthenes.	18·0	30·0	40·0	35·0	44·5	38·0	37·5	51·5	17·5	41·5
Unsaturateds	0·5	0·5	0·5	0·5	0·5	1·0	1·0	0·5	2·5	2·5
Paraffins .	78·5	65·0	49·0	59·5	50·5	43·5	49·5	29·0	69·0	35·0

If the Kauri-butanol value is accepted as a criterion of solvent power for comparison purposes, the following table, computed on a basis of benzene = 100, is enlightening. The spirits with boiling ranges lower

than that of white spirit also have appreciably lower Kauri-butanol values.

KAURI-BUTANOL VALUES OF PETROLEUM SOLVENTS

Grade	Kauri-butanol Value	Grade	Kauri-butanol Value
S.B.P. No. 1	27·5	White spirit	41·5
,, ,, 2	31·9	Benzene	100·0
,, ,, 3	33·3	Toluene	91·9
,, ,, 4	29·4	Xylenes	85·3
,, ,, 5	31·1	Cyclohexane	54·0
,, ,, 6	35·4	*n*-Heptane	24·8
Rubber solvent	37·4		

Coal-tar Hydrocarbons

Coal tar is as prolific as crude petroleum in providing raw materials for use in the varnish industry. Coal tar, modified by the addition of solvent, is used as an anti-corrosive black lacquer for iron work, and other valuable raw materials derived from it include: benzol, toluol, xylol, naphthas, coumarone, indene, diphenyl, creosote oil, anthracene oil, phenols, cresols and naphthalene. The last-named product is particularly valuable in that it is the starting material for phthalic anhydride manufacture. The benzol, toluol, xylol and naphthas are contained in the distillate fraction boiling below 210° C. Creosote oil occurs in the fraction boiling below 270° C. and anthracene oil boils above 270° C. Benzol and toluol are also recovered from coal gas itself, by absorbing them in creosote oil in scrubbers. They are regenerated subsequently from the creosote oil by ordinary or steam distillation. The light oil distillate from coal tar, from which the solvents are derived, is estimated to contain at least 200 different chemical compounds.[146] In addition to benzol, toluol and xylol it contains, among other substances, ethylbenzene, propyl benzene, coumarone, indene, pseudocumene, mesitylene, and ethyl *p*-xylene.

Benzol.—Benzol is the lowest boiling member of the aromatic hydrocarbons from coal tar, and because of its penetrating odour, toxicity and low flash-point, it is used considerably less than either toluol or xylol. Its most popular use is in the manufacture of paint removers because of its exceptional solvent power. Other uses are in rubber solutions and adhesives.

Commercial benzol is described according to the terms 90 per cent, 50 per cent, etc. Sometimes the description is merely 90° and 50°. These terms have nothing to do either with the benzene content of the solvent or its boiling range. A 90 per cent or 90° benzol is a solvent, 90 per cent of which distils below 100° C. Since the boiling-point of pure benzene is 80° C. it is, at once, apparent that commercial benzols are complex mixtures. Impurities likely to be present in commercial benzols

are carbon disulphide, toluol, xylol, thiophene, paraffin hydrocarbons, pyridine and acetonitrile.

Benzol is apt to freeze in cold weather and this should be prevented by storing under warm conditions. Benzol is an excellent solvent for drying oils, natural, polymerised or blown; for rubber, whether crepe or chlorinated, for rosin, ester gum, limed rosin, abietates, damar, mastic, run copals, copal ester, modified phenolic resins, maleic resins, coumarone, thiourea resins, long and short oil alkyds, petroleum, natural and coal-tar pitches, many metallic soaps and ethyl cellulose. Benzol does not dissolve shellac or soft Manila.

Toluol.—After benzol, toluol comes next in order of boiling range and evaporation rate. It is not a common solvent in varnish manufacture, where its chief use is in certain synthetic resin compositions, more particularly those containing alkyds. The bulk of toluol is used in the manufacture of cellulose lacquers.

Like benzol, toluol is a complex mixture, and commercial toluol contains benzol, xylol and traces of thiotolene. Its solvent power is very similar to that of benzol in that it readily dissolves the same types of compound.

Xylol.—Xylol is the most useful and best solvent of all the coal-tar hydrocarbons, including the naphthas. Its evaporation rate is not too fast, and it does not possess the toxicity of benzol. It is, moreover, free from the high boiling, slowly evaporating constituents of heavy naphthas. It is a very valuable solvent for synthetic compositions where white spirit has insufficient solvent power. Thus it is used in compositions containing hard modified or pure phenolic resins, especially if of the short oil type, in hard maleic resin-short oil compositions, for short oil alkyds, or for alkyds used in conjunction with urea-formaldehyde resins, for coumarone resin solutions where stability of solution is of paramount importance, for solutions of metallic soaps like those of aluminium and cerium which demonstrate strong gelling characteristics, and for chlorinated rubber lacquers. Often blends of xylol with white spirit yield mixtures of sufficiently good solvent power to accommodate the above-mentioned types of product. Xylol is very suitable for materials which are sprayed.

In commercial xylol one may expect to find *o*, *m*, and *p*-dimethyl benzenes, of which the meta variety will predominate in coal-tar xylol, toluol, trimethyl benzenes and ethyl benzene. Xylol has similar solvent properties to those of benzol.

Coal-tar Naphthas.—The naphthas are less refined solvents than benzol, toluol and xylol, and are primarily used because of their comparative cheapness. The better grades are used in place of xylol for the many purposes already enumerated, and in naphtha stains which have very good penetrating properties in wood without raising the grain. Naphthas are occasionally encountered in paint removers, where a cheap aromatic solvent is required with a lower evaporation rate than that of benzol or toluol. Various types of naphtha are available, from special

high flash naphthas of good colour and evaporation rate, to the cruder type as typified by heavy or solvent naphtha. Low boiling fractions are normally absent from commercial naphthas, but naphthas containing fractions with boiling ranges below 100° C. are available. An example of a naphtha, containing both low and higher boiling constituents, described as light solvent naphtha, has a boiling range of 60°–165° C. A light solvent naphtha described by Durrans has a boiling range of 110°–160° C., and is stated to consist chiefly of toluene, *o*, *m*, and *p*-xylenes, ethyl benzene and propyl benzene. Heavy solvent naphtha (b.p. 160–190) contains very little toluol or xylol, and consists chiefly of indene, coumarone, pseudocumene, mesitylene and durene.[147] Neumann describes two solvent naphthas, one in which the main constituent is xylol, with some cymene and a little toluol, and the other in which the main constituent is cymene, with some xylol and a little naphthalene oil.[148]

The smell of heavy solvent naphtha is very penetrating and objectionable, even when used in admixture with other solvents. It is also often lachrymatory. The light solvent naphthas enjoy a much wider popularity.

By comparison with petroleum hydrocarbons, coal-tar hydrocarbons are much superior in solvent power, yielding varnishes of greater stability and reduced viscosity. Kenny records that the higher boiling coal-tar fractions are effective in preventing the gelation of synthetic varnishes.[149]

Turpentine

Turpentine and rosin come from the same widely separated places throughout the world, wherever trees yielding the oleoresin thrive. Turpentines available are those from America (Carolina, Georgia, Alabama, Virginia), Finland, Sweden, France, Portugal, India, Greece, Russia, Spain, Mexico, British Honduras and the East Indies. Details of turpentine from a German source and from around the Amazon have been recorded. The bulk of the world's turpentine production originates from the United States of America. According to Lanorville, 67 per cent of the turpentine comes from the U.S.A. and 20 per cent from South-Western France.[150] This was at the period around 1936. A prediction made in 1923 that the turpentine supply from the United States would be exhausted in ten years has been completely confounded.[151]

Turpentine is obtained chiefly by three methods. The first involves the distillation of the oleoresinous exudation from the pine tree, from which rosin is obtained also, as described elsewhere. The second method involves distillation from wood chips by means of saturated or superheated steam before the subsequent extraction of wood rosin; or the distillation and fractionation of the solvent extract of wood chips. Sometimes the wood is destructively distilled in order to make it yield its volatile constituents. The types of turpentine are distinguished in that the former is known as gum spirits of turpentine, spirits of turpentine or balsam turpentine, and the latter types as wood turpentine—steam or destructively distilled. In obtaining turpentine from oleoresin, the

distillation is conducted often in the presence of a little water which distils over with the turpentine. When use is made of steam during the distillation of turpentine it may be used at high, normal, or low pressures.[152] Alcohol may replace water. Another method of refining crude turpentine involves the use of nascent hydrogen followed by treatment with activated charcoal and calcium chloride.[153]

When the turpentine is derived from the resinous exudation it is sometimes called "live" turpentine. If it is obtained from the wood or roots it is called "dead" turpentine.

The yield of turpentine from the tree is increased by the application of concentrated sulphuric and hydrochloric acids to the incision.[154]

Garvie [193] has explained that the liquid extract from pine stumps has a complex composition, as indicated by an extended boiling range 150°–240° C.). This, on careful fractionation, yields turpentine, di-(pentine, pine oil and other products.

Steam distilled wood turpentine is obtained from the turpentine fraction by first neutralising the formic, acetic and other acids in it, by vigorous mechanical agitation with fairly strong caustic soda solution. The alkali also affects the polymerisation of constituents with unpleasant smells. The final product is obtained by steam distillation at reduced pressure.

Turpentine of yet another type is known as cellulose sulphate or sulphite turpentine, and this is becoming increasingly important. It is obtained in the manufacture of pulp from pine wood during the boiling process, in which it is carried over with the steam. The chief constituents of sulphate turpentine are α- and β-pinenes, with some methyl sulphide and mercaptan, and it is these sulphur compounds which give it the pronounced smell. Sulphite turpentine contains cymene, a sesquiterpene and diterpene.[155] The physical constants of sulphate turpentine have been recorded as: boiling range 152°–175° C.; sp. gr. 0·864–0·866 (15° C.); and R.I. —1·4715–1·4727.[156]

The compositions of turpentines from different sources vary considerably, and these variations cause pronounced differences in both chemical and physical properties. Technical Bulletins 276 and 596, of the U.S. Dept. of Agriculture provide information on the compositions of gum and steam distilled turpentines. Gum turpentine contains 95 per cent pinene, divided into α and β types in the ratio 2 : 1. There is practically no β-pinene in steam distilled turpentine which consists of 98 per cent terpenic hydrocarbons, subdivided into 80 per cent α-pinene, the remainder consisting of limonene, dipentine, terpinene, terpinolene, etc.

Further information has been given on Russian turpentine by Rudakov and Artamonov,[164] and on German turpentine by Wienhaus, Ritter and Sanderman.[165]

The comparative properties of British, American, German and Indian turpentines, as required by their respective specifications, are given in the table on page 293.

COMPOSITION OF TURPENTINES

Source or Description.	*Composition.*
U.S.A. gum turpentine	*d*-α-Pinene (chiefly). β-Pinene (nopinene). Sylvestrene. Camphene. Dipentene.[157] (Old turpentine may contain camphoric anhydride, formic and acetic acids.)
U.S.A. steam distilled wood turpentine	(1) Limonene (dipentene) (chiefly). Pinene. *p*-Cymene. (2) α-Pinene (chiefly).[158] β-Pinene. α-Terpinene. γ-Terpinene. Limonene. Terpinolene.
France	*l*-α-Pinene.[159] *l*-β-Pinene.
Cuba	*l*-α-Pinene.
German balsam turpentine	α-Pinene (chiefly).[160] *Carene.* Nopinene.
India	Δ^3-Carene. β-Pinene. *d*-Longifolene. A Sesquiterpene.[157]
Russian	*d*-Δ^3-Carene (chiefly).[161] *d*-Sylvestrene. Δ^4-Carene. Pinenes. (Sylvestrene is given as the chief constituent elsewhere.[162])
Swedish	*d*-Δ^3-Carene (chiefly).[161] Δ^4-Carene. Pinenes.
Finnish	*d*-Δ^3-Carene (chiefly).[161] Δ^4-Carene. Pinenes.
Greek	α-Pinene (chiefly).[159]
Spanish	*l*-α-Pinene. *l*-β-Pinene (nopinene).[159]
Portuguese	*l*-α-Pinene. *l*-β-Pinene (nopinene).[159]
Destructively distilled turpentine	Sylvestrene.[159] Borneol. Fenchyl alcohol. Cineol. Phenol (sometimes).
Wood turpentine	Sylvestrene.[163] *d*-Pinene. Dipentene. Limonene. Terpineol.

PROPERTIES OF BRITISH, AMERICAN, GERMAN AND INDIAN TURPENTINE

	British.*		American.		German.		Indian.[166]
Specification	B.S.S. 1936	B.S.S. 1936	A.S.T.M.	A.S.T.M.	R.A.L. 1927	R.A.L. 1927	—
Description	Type 1	Type 2	Balsam turpentine and steam distilled wood turpentine	Dry distilled wood turpentine	Balsam turpentine	Wood turpentine	Indian gum turpentine
Specific Gravity	0·862–0·872 (15·5° C.)	0·859–0·875 (15·5° C.)	0·860–0·875 (15·6° C.)	0·860–0·875 (15·6° C.)	0·855–0·872 (20° C.)	0·86–0·88 (20° C.)	0·862–0·870 (15·5° C.)
R.I.	1·469–1·478 (20° C.D.)	1·463–1·483 (20° C.D.)	1·465–1·478 (20° C.)	1·463–1·483 (20° C.)	1·467–1·468 (20° C.)	1·465–1·478 (20° C.)	—
Flash-point	$\not< 90°$ F.	$\not< 90°$ F.	—	—	—	—	98° F.
Boiling range	$\not> 1$ % by vol. below 150° C. $\not< 95$ % by vol. below 170° C.	$\not> 1$ % by vol. below 150° C. $\not< 70$ % by vol. below 170° C. $\not< 90$ % by vol. below 180° C.	First drop 150°–160° C. $\not< 90$ % by vol. below 170° C.	First drop 150°–157° C. $\not< 60$ % by vol. below 170° C. $\not< 90$ % by vol. below 180° C.	First drop 152°–156° C. $\not< 75$ % below 162° C.	First drop 150°–165° C. $\not< 75$ % below 180° C.	First drop 150° C. $\not< 90$ % below 170° C.
% by vol. unpolymerisable with conc. H_2SO_4	$\not> 11$ %	$\not> 16$ %	$\not> 2$ %	$\not> 2$ %	$\not> 2$ %	$\not> 2·5$ %	
R.I. of unpolymerisable	Not below 1·490 at 20° C.	Not below 1·480 at 20° C.	Not below 1·5 at 20° C.	Not below 1·48 at 20° C.	Not below 1·5 at 20° C.	Not below 1·48 at 20° C.	

* Abstracted by permission from British Standard Specification, Turpentine, 1936, official copies of which can be obtained from the British Standards Institution, 28 Victoria Street, London, S.W.1.

Turpentines in which pinenes predominate do not undergo atmospheric oxidation so readily as those where Δ^3-carene is the principal constituent. For this reason Indian turpentines are said to be inferior to both American and French turpentines. The Δ^3-carene and the longifolene which it contains both accentuate the tendency to oxidation, and increase the non-volatile content.[157] Results of experiments on the comparative rates of oxidation of *d*-α-pinene and *d*-Δ^3-carene in air and oxygen have been recorded by Simonsen.[161] These show clearly the increased oxidation with carene. Krestinskii and Eshchenko had reported similar findings earlier.[167] The rate of oxidation can be reduced by additions of anti-oxidants, such as resorcinol or pyrogallol, of which pyrogallol is the more effective. With these anti-oxidants present carene still exhibits a marked tendency to oxidation which, under these conditions, also, is more pronounced than with pinene. Anti-oxidants almost completely inhibit the oxidation of pinenes. Russian turpentine, by reason of its carene content, would oxidise more readily than American turpentine.

Turpentines from different sources have characteristic smells. Thus it is possible to distinguish between American, French and Indian grades. American wood turpentine can be distinguished often from gum turpentine by smell.

Turpentine obtained by destructive distillation is claimed to have better solvent power than either gum or steam distilled turpentine,[168] but whereas either of the two latter types are quite suitable for the manufacture of paints and varnishes and are used extensively for these products, destructively distilled turpentine is rarely used. It suffers from an inconvenient acidity and a tendency to resinify. Gum turpentine is perhaps more popular than wood turpentine in the U.K., but wood turpentine is consumed in large quantities in America as a paint and varnish thinner.

The optical activity of turpentine obtained from the same *P. pinaster* tree, remains substantially constant over long periods, although variations are observed in the turpentines from different trees.[169]

A tree, *Nectandra elæophora*, native to the district around the Amazon, yields a volatile oil on incision. It resembles in many ways the oleo-resinous exudation from which turpentine is derived. The volatile oil obtained has a b.p. 156°–274° C., and when fractionated yields a fraction b.p. 156°–179° C., sp. gr. 0·886 (15° C.), R.I. 1·465 and flash-point 40° C. This so closely resembles ordinary turpentine that it is suggested as a substitute. A fraction, b.p. 180°–230° C., sp. gr. 0·908 (15° C.), R.I. 1·471 and flash-point 58° C., is similar to pine oil.[170]

Camphor oil, which contains pinene, camphene, limonene, dipentene, cineol and phellandrene, may be used as a turpentine substitute. Davidsohn and Davidsohn give for it a boiling range of 175°–200° C. and a sp. gr. 0·860–0·910 (15° C.).[171]

Because of its unsaturation turpentine has a high iodine value. It is interesting to note, however, that in spite of its tendency to oxidise, little change in iodine value occurs during normal storage.[172]

	I.V. (*Hanus*)
Fresh American turpentine	220
Old American turpentine	218
Fresh French turpentine	213
Old French turpentine	216

Chadwick and Palkin have provided information on the composition of the less volatile portion of gum turpentine. Its approximate composition is 40 per cent monocyclic hydrocarbon, 20 per cent terpene alcohols and phenols, and 40 per cent distilling above 85° C./10 mm., consisting chiefly of esters and ethers.[173]

Turpentine has better solvent power than white spirit for most varnish constituents. It dissolves drying oils both treated and untreated, rosin, ester gum, copal ester, limed rosin, damar, metallic drying salts, modified phenolic resins, maleic resins, long and medium oil length alkyds and asphaltums. It is a useful constituent of chlorinated rubber compositions, but its use is not recommended with certain types of hard phenolic resin.

Because of the readiness with which it attacks copper it is not used as a thinner for impregnating insulating varnishes or for bronze paint media. Turpentine is added to spirit varnishes to improve their adhesion on greasy surfaces.

Oxidised Turpentine.—In the past, oxidised turpentine attracted some attention and many claims were made for it. When it is oxidised in bulk its viscosity increases. Oxidised turpentine or fat oil, as it is sometimes called, is made by heating the turpentine at 145° C. in the presence of air. The product is reduced to a quarter of its original volume by steam distillation. So-called oxidised turpentine is obtained during the distillation of pinene. Fat oil performs the dual rôle of a plasticising resin, in addition to conferring durability, gloss, and resistance to steam and ultra-violet light on lacquer films.[174] Its boiling range is higher than that for turpentine and its evaporation rate is slower. Oxidised turpentine has a boiling range of 165°–185° C.; sp. gr. 0·860–0·910 (15° C.); flash-point 40°–50° C.; R.I. 1·476–1·479 (20° C.).[175]

When turpentines containing pinenes are oxidised, peroxides, resin, and traces of formic acid and cymene are formed.[176] Other possible oxidation products include acetic acid, carbon dioxide, camphoric acid aldehyde, soberol and pinol hydrate.[177] The subject of peroxide formation in turpentines is discussed under "Driers and Other Metallic Soaps."

Polymerised Turpentine.—The use of sulphuric acid on turpentine as a polymerising agent has been mentioned already. Bleaching earths such as floridin, as well as silica gel and activated carbon, also have a polymerising action on turpentine, forming high boiling liquids. Experiments conducted on the action of bleaching earths on pinenes revealed that *l*-pinene was more reactive than the *d*-variety. Turpentines from different sources will react, therefore, according to the presence of these substances. Bleaching earths also have an action on pine oils. The

natural earth produces a heavy non-fluorescent oil, and activated earth gives a fluorescent oil.[178, 179]

Hydroterpins.—Hydroterpin is made by hydrogenation of turpentine. Sulphate turpentine has been hydrogenated also. This is accomplished by heating the liquid at 280°–400° C. with hydrogen under pressure in the presence of a catalyst. Catalysts suggested are metals of Group VI in the Periodic Table. Hydrogenated *p*-cymene and hydrocarbons of uncertain composition are formed.[180]

Hydroterpin has a slower evaporation rate than turpentine and a higher boiling range. Its physical constants are: sp. gr. 0·879/15° C.; boiling range 172°–200° C.; and R.I. 1·473–1·4760 (20° C.). Hydroterpin is not noticeably autoxidisable.

It is said to prevent rivelling of wood oil.

Dipentene.—Dipentene is a terpene, and is available in many states of purity. The pure substance boils at 175°–176° C., but commercial grades have much more extended ranges, 157°–192° C. being typical. Its evaporation rate is slower than that of turpentine. Comparative evaporation rates conducted at room temperature showed that with the volume of liquid taken, at six hours, dipentene showed only 22 per cent volatile against 70 per cent for wood turpentine. Dipentene undergoes polymerisation with sulphuric acid and 2–3 per cent unpolymerisable is usual. Specific gravity varies from 0·845–0·860/20° C. and R.I. from 1·472–1·477/20° C. Dipentene is autoxidisable. It has a characteristic smell.

Dipentene has excellent solvent power, and can be used with many types of natural and synthetic resins, including phenolic resins, alkyds, maleic resins and coumarone. It dissolves rubber also. It is useful for wood oil varnishes in that it prevents skinning. Small percentages with or without other anti-skinning agents are used in wood oil-phenolic varnishes for this reason. It is valuable with alkyds because of its improved solvent power compared with white spirit, and the fact that it aids brushing and confers good flow. Dipentene occurs as a solvent in some paint removers. Its good dispersing properties are utilised in short phenolic varnishes to prevent gelling during storage. The slow initial rate of evaporation is said to promote "through drying" rather than "surface drying," and hence rivelling is minimised. When dipentene replaces some of the commoner solvents an increase in drying time occurs, and it is suggested, on this account, that dipentene is used so that it constitutes not more than 25 per cent of the volatile portion.

Sometimes dipentene is recommended as a wetting agent. It reduces surface tension.[181]

Pine Oils.—As their name implies they are products of the pine tree. They are intermediate in properties between true solvents and true plasticisers. Old stumps and roots, in which the terpenes have become oxidised and hydrolised, yield pine oils on steam distillation. Other methods of obtaining pine oils are by extraction of pine stumps or dry distillation. According to Pickett and Schantz pine oil has the following

approximate percentage composition: α-terpineol 50–60; other terpineols 15–25; terpenes 5–10; borneol 5–10; fenchyl alcohol 5–10; esters 5–10; ketones and phenols 1–2.[182]

Among the other terpineols, β-terpineol may be present. Other components sometimes include α- and β-pinenes, limonene, dipentene, terpinolene, camphene, methyl chavicol, cineol, camphor, menthane and anethole.

Two types of pine oil are known commercially, the ordinary and the heavy grade. The heavy grade has a boiling range of 210°–220° C. and the former has a substantial portion boiling below 210° C.

Pine oils vary in colour from pale yellow to water white, depending upon the care taken in their distillation. They have excellent solvent properties, dissolving rosin, ester gum, copal ester, modified phenol resins, alkyds and coumarone. There is a slight but definite affinity for water. The evaporation rate is slow, and for this reason they are incorporated in varnishes and enamels especially of the alkyd type, to permit easy brushing over large surfaces, and to promote flow. They may be used in spraying compositions to assist levelling. Toch has advocated their addition to paints to assist penetration,[183] on wood. In paints, too, wetting and dispersion is improved and livering tendency reduced.

The pleasant smell of pine oils has caused them to be used as deodorants. Their valuable emulsifying and antiseptic properties make them popular constituents of soaps.

Rosin Spirit.—When rosin is distilled several fractions are obtained, among which are rosin oil and rosin spirit. The former has been considered in the section devoted to rosin. Rosin spirit is a solvent with a very extended boiling range (150°–300° C.). Its specific gravity varies from 0·890 to 0·940.

It is rarely used in varnish manufacture.

Solvenol.—Solvenol is a proprietary solvent of terpenic character, derived from pine wood oleoresin. It consists chiefly of dipentene but contains, in addition, pinene, terpinolene, terpinene, cymene and some terpene alcohols. It has superior solvent power to that of turpentine, and is frequently used in admixture with white spirit to improve both solvent power and smell. Compared with turpentine its tendency to oxidation is less. Its evaporation rate is also less.

Among many advantages claimed for it are its properties of improving gloss, dry, adhesion, wetting, flow, and resistance to skinning.

Terpinolene.—Terpinolene is one of the constituents of pine oil. It has been used as a substitute for Solvenol, but although its solvent power is good its evaporation rate is slower.

Terpene Ethers

New solvents of this type are now available under the trade name of "Terposol." These additive terpene ethers are produced by the interaction of α- and β-pinenes with alcohols.[195]

Terposol 3, is a colourless liquid, boiling range 200°–225° C., and consists of a mixture of 70 per cent terpinyl methyl ether and 30 per cent terpineols. It can be used as a wetting agent in varnishes and enamels, and is similar in some respects to pine oil, although it lacks its solvent power.

Terposol 8, has a higher boiling range, 245°–290° C., which places it in a class between the usual volatile solvents and the commonly accepted plasticisers. It consists substantially of a mixture of mono and diterpinyl ethylene glycol ethers with a small amount of terpinyl methyl ethers. Because of its strong solvent power it has been suggested as a constituent of paint removers.

Other Hydrocarbons

Decalin.—Chemically this is decahydronaphthalene. It is an inert solvent because it is completely saturated. By comparison with most other solvents used for varnishes it is a pure material, possessing a close boiling range of 183°–192° C. It can be used wherever white spirit is used, with the added advantage of improved solvent power. According to Kauri butanol tests its solvent power is equivalent to that of turpentine. Its evaporation rate is slower than that of turpentine or white spirit, and for this reason it is sometimes substituted for them in brushing alkyd varnishes, to facilitate brush application over large surfaces, and to improve the flow. Solutions of metallic soaps, prepared in Decalin, are claimed to have better stability than corresponding white spirit solutions. This is said to be the case with cobalt linoleate solutions.[184]

Tetralin.—Except that tetrahydronaphthalene and decahydronaphthalene are both hydrogenated products of naphthalene, there is little else in common. Tetralin is unsaturated but Decalin is completely saturated. Because of its different chemical constitution, Tetralin darkens on storage in contact with air due to oxidation, a characteristic which is absent with Decalin. The evaporation rate of Tetralin is generally considered too low to permit its general use in air-drying finishes, and it finds application in stoving finishes. It is found sometimes in air-drying finishes to improve flow and brushability. Because of its exceptional solvent power, far superior to that of Decalin or turpentine, it is used in paint removers.

Further evidence in support of its outstanding solvent power is that, when mixed with white spirit, it yields more stable solutions with short oil alkyds than similar xylol and white spirit blends.[185].

It is sometimes incorporated in chlorinated rubber varnishes to eliminate the "cobwebbing" tendency of these products when sprayed. Another property attributed to Tetralin is its effect in reducing wrinkling of tung oil varnishes. It is not advisable to use Tetralin in media for white or delicately tinted enamels. There is its natural tendency to yellow, and also the possibility of it exaggerating the pink colour of manganese driers when these are used.

The properties of turpentine, Tetralin, Decalin and white spirit have been compared thoroughly by Smith.[185]

Tetralin is a solvent for drying oils in their various forms. It has been stated that Tetralin dissolves linoxyn.[151] Rosin, ester gum, copal ester, modified phenolic resins, coumarone, alkyds, mastic, rubber, chlorinated rubber, waxes and pitches, are all dissolved by Tetralin. Natural copals, shellac, phenol formaldehyde and urea formaldehyde resins are insoluble.

Cymene.—Sources of cymene are the oxidation products of turpentine, sulphite turpentine, and American wood turpentine. It may be produced also by the heat treatment of turpentine in the presence of iodine. Chemically it is isopropyl-*p*-methyl benzene.

Cymene has rather better solvent power than turpentine, and has been used to a small extent as a substitute for it in varnishes. It is a good solvent for varnish making oils and resins. Unlike turpentine it has little tendency to oxidise. Because of its greater softening action it may lift undercoats, especially during application by brush. Its smell is characteristic but not unpleasant. One of the main factors militating against its more general use as a varnish thinner is its cost.

Cumene.—Cumene, or isopropyl benzene as it is described chemically, is a good solvent for resins and oils. When pure it has a boiling-point of 152° C. which makes it interesting as a possible varnish thinner. It has not attracted much attention as yet.

Hydrogenated Naphthas.—These are derived from petroleum hydrocarbons. Crude petroleum is extracted with sulphur dioxide and the extracts subjected to hydrogenation. The hydrogenation is conducted at high temperature in the presence of catalyst.[186] A protected process is described, in which hydrocarbon oils with boiling-point up to 370° C. are subjected to hydrogenation and limited oxidation at pressures above 50 lb. per sq. in.[187] Low aniline point gas oils are reacted with hydrogen at 370°–450° C. in the presence of a catalyst.[188]

Hydrocarbons of improved solvent power are obtained from Californian petroleum by a selective solvency process. Aromatic hydrocarbons are derived from petroleum also, as a result of molecular rearrangement by subjecting it to pyrolytic processes.[189]

The properties of hydrogenated naphthas vary with boiling range. Solvent power, dimethyl sulphate value, specific gravity and flash-point, all increase with boiling range as shown by the following tables.[188, 186]

TABLE I

	Boiling Range (°C.).	Sp. Gr.	Flash-point (°F.).	Aniline-point (°C.).	Kauri Butanol Value.
1.	93–135	0·7932	60	8	66·5
2.	135–185	0·8565	80	−27	74·0
3.	185–215	0·8899	140	−30	77·8
4.	215–288	0·9484	150	−41	90·0

TABLE II

	Boiling Range (°C.).	Flash-point (°F.).	Dimethyl Sulphate Value.
1.	93–135	below 60	24%
2.	135–185	61	62%
3.	185–215	135	87%
4.	215–238	190	100%

The evaporation rates of the naphthas in Table I would be in the approximate ratios : 1 : 4 : 33 : 36.

For solvent power they are superior to petroleum hydrocarbons and compare favourably with the aromatic solvents. Figures given by Kelly [188] demonstrate the solvent powers of hydrogenated naphtha, petroleum naphtha and coal-tar naphtha.

	Sp. Gr. (60° F.).	Aniline-point.	Kauri Butanol Value.	Boiling Range (° C.).
Hydrogenated naphtha .	0·8676	−28·3	77	145–211
Petroleum naphtha . .	0·7715	64	30	155–212
Coal-tar naphtha . .	0·859	8·3	72	150–192

Hydrogenated naphthas dissolve most of the normal varnish constituents easily, and are recommended for use where solvents with better solvent power than white spirit are necessary. They are valuable, therefore, in phenolic resin varnishes and for alkyds, and in these types of product they can replace coal-tar naphthas and turpentine. They are solvents for rubber and may be incorporated in paint removers. Furthermore, they have good wettability for pigments. They may be obtained with low sulphur contents.

Tar Spirit.—Tar spirit is a crude solvent of very variable composition. The quantity used in varnish manufacture is small and the bulk of it is distilled in Norway. It is usually reddish-brown in colour, and a good sample should be free from suspended matter. Special rectified tar spirits are available of improved colour. The smell is characteristic and very penetrating. High concentrations of vapour such as those accumulating during thinning, without adequate ventilation, are objectionable because of their irritant effect on the eyes.

Tar spirits have very extended boiling ranges, and the lower boiling fractions confer inconveniently low flash-points on the solvent. They should be tested for flash-point carefully in order to avoid risk during thinning. Tar spirits with initial boiling-points below 120° C. should become suspect for flash-point.

Because of their very variable composition, tar spirits exhibit wide variations in physical constants, for example, specific gravity varies from 0·900–1·050 (15° C.).

Tar spirits are naturally acidic in character, and the acidity is of such a nature that in some instances it has been sufficient to cause serious disintegration of iron storage containers. The acidity using phenol phthalein as indicator should not exceed 30.

Tar spirits have excellent solvent power. They find application chiefly in black bituminous stoving enamels and in paint removers.

Alcohols

These are a very important class of varnish solvents. Of the series available, ethyl and butyl alcohols are the most important, with methyl and amyl alcohol used in much smaller quantities.

Ethyl Alcohol.—This alcohol is available in several forms. The most popular form for the manufacture of spirit varnishes, etc., is known as industrial methylated spirits. This comprises 95 per cent by volume of ethyl alcohol and 5 per cent by volume of methyl alcohol or wood naphtha. Some water is present also and the alcohol is sold in the following grades: 61 O.P., 64 O.P., 66 O.P., 68 O.P. and 74 O.P. 64 O.P. is the grade most commonly used for spirit varnishes, and alcohols with higher overproof number are used only for special purposes.

Specific Gravity at 60° F.	% Alcohol by Weight.	% Alcohol by Volume.	% Over Proof.
0·8295	87·38	91·31	60·02
0·8275	88·16	91·90	61·05
0·8255	88·96	92·51	62·12
0·8235	89·73	93·09	63·13
0·8215	90·46	93·62	64·06
0·8195	91·18	94·13	64·96
0·8170	92·07	94·76	66·07
0·8150	92·81	95·29	67·92
0·8130	93·55	95·82	67·92
0·8105	94·45	96·43	69·00
0·8080	95·32	97·02	70·03
0·8055	96·20	97·62	71·07
0·8030	97·03	98·16	72·02
0·8005	97·87	98·69	72·95
0·7975	98·81	99·26	73·97
0·7945	99·78	99·86	75·01
0·7938	Absolute alcohol		75·25

Another type of alcohol is toilet industrial methylated spirit, and it is similar to the ordinary industrial methylated spirit already described, except that the denaturant is carefully selected. Pyridinised methylated spirit contains a trace of crude pyridine and is sold in 61 O.P. and 64 O.P. strengths.

Mineralised methylated spirit is a more complex mixture than any of the foregoing. Apart from the fact that it is tinted violet, it has a larger wood naphtha content, and contains, in addition, some mineral naphtha and pyridine. It is available in 61 O.P. and 64 O.P. strengths.

Varnish Constituents

Ethyl alcohol is a good solvent for many varnish or lacquer resins, including shellac, accroides, spirit Manila, sandarac, elemi, rosin, gum thus, mastic, damar, and phenol formaldehyde resins. It does not dissolve the drying oils. It is, however, a good solvent for castor oil.

In addition to its use in spirit varnishes of all types, industrial alcohol is used as a part solvent in paint removers.

n-*Butyl Alcohol.*—Butyl alcohol has many of the properties of ethyl alcohol except that its evaporation rate is considerably slower. It is frequently used in conjunction with the latter to eliminate blushing tendency and to aid flow and spraying. It is claimed to reduce the surface tension of spirit varnishes. Butyl alcohol in small additions is a valuable coupling solvent, and is used to reduce the viscosity of solutions of metallic soaps and alkyds. With respect to solvent power butyl alcohol is similar to ethyl alcohol in that it is a solvent for shellac, spirit Manila, sandarac, elemi, damar, phenol formaldehyde resins and castor oil.

Durrans points out that it dissolves hard copals, including Congo and Kauri, as well as ester gum and linseed oil.[191] Butyl alcohol is a common solvent for use with urea formaldehyde resins.

Amyl Alcohol.—Amyl alcohol is rarely used as such in spirit varnishes. Whenever it is deemed to be necessary to use this type of solvent it is generally in the form of fusel oil. Amyl alcohol is introduced to eliminate blush. Its solvent properties are similar to those of butyl alcohol, but it has a lower evaporation rate.

Neither the smell of amyl alcohol nor that of fusel oil is very pleasant, and because of the low volatility of these solvents it is persistent. Their unpleasant smell has undoubtedly militated to some degree against an extension of their use.

Fusel oil of good type is water white in colour. Cruder types are pale yellow. Fusel oil is a complex mixture consisting chiefly of alcohols, of which the following are present: amyl and isoamyl alcohols, propyl and isopropyl alcohols and normal, iso and tertiary butyl alcohols. Some aldehydes and esters may be present also. The existence of normal butyl alcohol in fusel oil is doubtful.

Methyl Alcohol.—This solvent has not enjoyed much popularity, probably because of its toxicity. Methyl alcohol is a good solvent for shellac, rosin and phenol formaldehyde resins of the bakelising type. Like ethyl alcohol it dissolves castor oil. It does not dissolve linseed oil. It is highly volatile and its high volatility stimulates blushing.

Ketones

Acetone and methyl ethyl ketone are the two chief ketones used, and their outstanding solvent powers make them valuable constituents of the inflammable type of paint removers. Their main disadvantages are their extremely low flash-points. Both solvents are very volatile, and methyl ethyl ketone is the less volatile of the two. Where lower volatility still is

required, methyl butyl, methyl propyl, or methyl amyl ketones are suggested. Acetone and methyl ethyl ketone dissolve rosin, ester gum, copal ester, alkyds, vinyl resins, and both drying oils and castor oil.

Chlorinated Hydrocarbons

Chlorinated hydrocarbons have excellent solvent power for most varnish constituents. The low boiling members are too volatile for general use and their toxicity has limited their use also. Some chlorinated hydrocarbons possess the peculiar characteristic of instability under certain conditions of storage, and tend to attack metal containers. Sealed galvanised drums are satisfactory for methylene chloride. Their greatest advantage apart from solvent power is their non-inflammability. Methylene chloride, one of the least toxic of the series, is found as the chief constituent of non-inflammable paint removers. Other hydrocarbons which have been used in paint removers are : carbon tetrachloride, tetrachlorethane, ethylene dichloride, dichlorethylene and the dichlorbenzenes.

In fireproof varnishes and compositions, such as for the production of insulating sleeving, chlorinated hydrocarbons may be incorporated with advantage, for the dried films retain traces of solvent for long periods, and if the solvent is of the non-inflammable type it will help to confer temporary non-inflammability on the film.

Matt spirit varnishes include monochlor and dichlorbenzene to produce mattness.[192] Rapid drying bituminous compositions for brewer's vats are thinned with chlorinated hydrocarbons.

The Nitroparaffins

The nitroparaffins constitute a new group of solvents which are available commercially. The members of the series in which the varnish trade is interested, include nitromethane, nitroethane, 1-nitropropane and 2-nitropropane.

A very interesting feature of these solvents is that their flash-points (Tag open cup) come within the range 103°–120° F., which is comparatively high for boiling range limits of 101°–132° C. The use of some of the other strong solvents has been restricted because of their unpleasant odours—those of the nitroparaffins are mild and inoffensive. Full details of the physical constants are included in the table of Constants of Solvents.

They fill a useful niche with regard to their solvent power, for they dissolve a number of varnish constituents, which hitherto have presented some difficulty. The 1- and 2-nitropropanes dissolve road tar, pure phenolic resins like Beckacite 1001, coumarone resins, alkyds, vinyl chloride and acetate polymers and the co-polymers, acrylic resins, urea resins, chlorinated rubber, benzyl and ethyl celluloses ; and the acetobutyrate, acetopropionate, triacetate and nitrate of cellulose. The nitroparaffins are, in addition, good solvents for drying oils in their various forms, and for most other common varnish constituents.

Their good solvent power will be exploited in special paint removers for synthetic finishes.

The Chloronitroparaffins

A whole series of chlorinated nitroparaffins have been made available as powerful solvents for fats, waxes, and the like. They have a very convenient boiling range, 120°–144° C., and, of course, their flash-points are high.

They are especially recommended as anti-gelling agents for rubber cements and some of them are valuable as fumigants. Full details of their physical properties are included in the table of Constants of Solvents.

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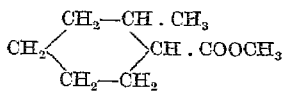
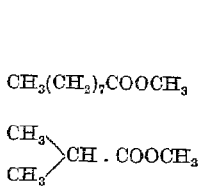
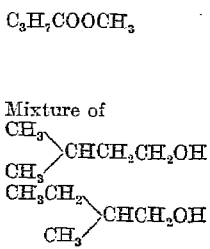
CONSTANTS OF SOLVENTS AND DILUENTS

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (°C.).	M.Pt. (°C.).	S.G.	Flash Point (°F.).	R.I.	Vapour Pressure (mm.).
ACETALS									
Acetal	Dissolvan	$CH_3CH(OC_2H_5)_2$	118	104		0·831 (20° C.)		1·38	
Dimethyl acetal		$CH_3CH(OCH_3)_2$	90	64		0·879 (0° C.)			
Ethylal		$CH_2(OC_2H_5)_2$	104	88		0·840 (0° C.)			
Methylal		$CH_2(OCH_3)_2$	76	42	−104	0·872 (15° C.)			
ACETATES									
Allyl acetate		$CH_2{=}CHCH_2COOCH_3$	100·0	103		0·928		1·4045	
Amyl acetate	Pentasol acetate Pentacetate	$C_5H_{11}COOCH_3$	130·1	120–145		0·872 0·880	87		
Amyl acetate sec.		$CH_3CH_2CH_2CH(CH_3).COOCH_3$	130·1	125–135		0·86			
Amyl acetate iso		$(CH_3)_2CH(CH_2)_2COOCH_3$	130·1	140–142	−78	0·87	77	1·402	
Benzyl acetate	Plastolin I	$C_6H_5CH_2COOCH_3$	150·1	215	−51·5	1·061	200	1·502 1·5232	
Butyl acetate	Tamasol	$C_4H_9COOCH_3$	116·1	126	−77	0·883 (20° C.)	88 78	1·395 (25° C.)	10 (20° C.)
Butyl acetate sec.		$(CH_3)(C_2H_5)CHCOOCH_3$	116·1	112		0·865		1·3915 (20° C.) 1·3866 (25° C.)	29 (30° C.)

Butyl acetate iso	Tamasol J	$(CH_3)_2CHCH_2COOCH_3$	116·1	116		0·870	64 68	1·392	13 (20° C.) 27 (30° C.)
Cyclohexyl acetate	Hexalin acetate Adronal H.A. solvent	$C_6H_{11}OCOCH_3$	142	170–176		0·947 0·950	149 155 156	1·439	7 (30° C.)
Diethylene glycol monoethyl ether acetate	Carbitol acetate	$C_2H_5OCH_2CH_2OCH_2CH_2COOCH_3$	176·1	218		1·012 (20° C.)	225	1·423 (20° C.)	<0·1 (20° C.)
Diethylene glycol monobutyl ether acetate	Butyl carbitol acetate	$C_4H_9OCH_2CH_2OCH_2CH_2COOCH_3$	204·2	236–249		0·987 (20° C.)			<1 (30° C.)
Ethyl acetate	Essigester Lactonal	$C_2H_5COOCH_3$	88·1	77	−82	0·901 (20° C.)	31	1·373	73–76 (20° C.)
Ethylene glycol monomethyl ether acetate	Methyl Cellosolve acetate	$CH_3OCH_2CH_2COOCH_3$	118·1	143		1·005 (20° C.)	111 132		3 (20° C.)
Ethylene glycol monoethyl ether acetate	Cellosolve acetate	$C_2H_5OCH_2CH_2COOCH_3$	132·1	156		0·975 (20° C.)	117 142	1·405	1·25 (20° C.)
Ethylene glycol monoacetate		$CH_3COOCH_2CH_2OH$	104·1	185–195		1·11	215		
Ethylene glycol diacetate		$CH_3COOCH_2CH_2COOCH_3$	146·1	190	−31	1·15		1·415	
Ethylene glycol monobutyl ether acetate	Butyl cellosolve acetate	$C_4H_9OCH_2CH_2COOCH_3$	160·1	188–192		0·943 (20° C.)			<1 (30° C.)
Furfuryl acetate		$C_4H_3OCH_2COOCH_3$	140	175		1·1175 (20° C.)		1·4627	
n-Heptyl acetate		$C_7H_{15}COOCH_3$	158·1	191·5		0·874		1·4153	
n-Hexyl acetate		$CH_3(CH_2)_5COOCH_3$	144·1	169·2		0·890		1·4103	5 (30° C.)
1-Methyl pentamyl acetate				132–159		0·860 (20° C.) 0·865 (20° C.)		1·408	

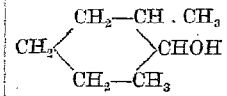
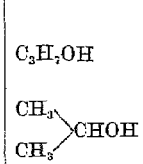
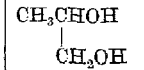
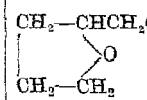
CONSTANTS OF SOLVENTS AND DILUENTS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (°C.).	M.Pt. (°C.).	S.G.	Flash Point (°F.).	R.I.	Vapour Pressure (mm.).
ACETATES (*cont.*)									
4-Methyl pentamyl acetate				136–146		0·856 (20° C.)	113	1·394	
Methoxybutyl acetate	Butoxyl	$CH_3OCH(CH_3)CH_2CH_2COOCH_3$	146	167–171		0·956 (20° C.)	140		
Methyl cyclohexyl acetate	Sextate. Methyl hexalin acetate		156	175–190		0·94 0·98	150 155 156		
Methyl acetate		CH_3COOCH_3	74·1	58	−98	0·957 (0° C.) 0·933	9 20	1·361	173 (20° C.)
Octyl acetate		$CH_3(CH_2)_7COOCH_3$	172·2	210	−38·5	0·873 (20° C.)	180		0·3 (20° C.)
Propyl acetate iso	Paracetat		102·1	89–91		0·930	32 35		45 (20° C.)
Propyl acetate		$C_3H_7COOCH_3$	102·1	102	−95	0·897	53	1·384	
ALCOHOLS									
Amyl alcohol (coml.)	Pentasol (synthetic product)	Mixture of  and	88·1	128–132	−134	0·816 (15° C.)	105 115	1·39	10 (20° C.)

Amyl alcohol (coml.)	Fusel oil			105–132		0·813 (15° C.) 0·819 (15° C.)	97		
Benzyl alcohol	Plastoform I	$C_6H_5CH_2OH$	108·1	205	−15	1·043 (20° C.)	287	1·540	<1 (30° C.)
Butyl alcohol		C_4H_9OH	74·1	116	−90	0·810 (20° C.)	97 111	1·396	5 (20° C.) 11 (30° C.)
Butyl alcohol iso	Isopropyl carbinol	$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CHCH_2OH$	74·1	108	−108	0·802 (20° C.)	100	1·396	10 (20° C.) 17 (30° C.)
Butyl alcohol sec.	Methyl ethyl carbinol Butanol 2	$CH_3CH(OH)C_2H_5$	74·1	99		0·819 (20° C.)	74	1·397 (20° C.)	26 (30° C.)
Butyl alcohol tert.		$(CH_3)_3COH$	74·1	83	25	0·780 (25° C.)			
1 . 3 . Butylene glycol		$CH_3—CHOH—CH_2—CH_2OH$	90·1	207		1·02 (20° C.)		1·442	
Cyclohexanol	Hydralin Adronol Hexalin Anol	$CH_2\!<\!\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}\!>\!CHOH$	100	160	22	0·945 (15° C.)	117 155	1·468 (20° C.)	2 (30° C.)
Diethylene glycol	Prestone	$HOCH_2CH_2OCH_2CH_2OH$	106·1	244		1·1185 (20° C.)	255 286	1·4475	<0·1 (20° C.)
Ethyl alcohol	Ethanol Ansol M. Spirits of wine	C_2H_5OH	46·1	78	−130	0·7938 (15° C.)	53 65 57	1·367	44 (20° C.) 78 (30° C.)
	74 OP					0·7975 (15° C.)			
	66 OP					0·8170 (15° C.)			

CONSTANTS OF SOLVENTS AND DILUENTS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (°C.).	M.Pt. (°C.).	S.G.	Flash Point (°F.).	R.I.	Vapour Pressure (mm.).
ALCOHOLS (*cont.*)									
Ethyl alcohol (*cont.*)	64 OP					0·8215 (15° C.)			
	61 OP					0·8275 (15° C.)			
	Mineralised meth.					0·825 (15° C.)			
	Pyridinised meth.					0·826 (15° C.)			
2 . Ethyl butyl alcohol		$C_2H_5CHC_2H_5CH_2OH$	102·1	149		0·833 (20° C.)	137	1·421	3 (20° C.)
Ethylene glycol	Glycol Losungmittel G	$\begin{array}{l} CH_2OH \\ \vert \\ CH_2OH \end{array}$	62·0	197	−11	1·116 (20° C.)	241		0·1 (20° C.)
Ethyl polyglycol				190–200		1·006 (20° C.) 1·010 (20° C.)	200		
Furfuryl alcohol		$\begin{array}{l} CH{=}C\,.\,CH_2OH \\ \vert \quad\quad \rangle O \\ CH{=}CH \end{array}$	98	169		1·135 (20° C.)		1·4864	2 (30° C.)
Hexyl alcohol		$CH_3(CH_2)_4CH_2OH$	102·1	144–156		0·833 (20° C.)		1·4229	4 (30° C.)
Methyl alcohol	Spiritogen Methanol Columbus spirit Methynol	CH_3OH	32·0	65	−95	0·796 (20° C.)	32 52 59	1·332	95 (20° C.) 160 (30° C.)

Methyl alcohol	Wood spirit Wood alcohol Wood naphtha	Consists chiefly of 80 % or more CH_3OH with $(CH_3)_2CO_3$, CH_3COOCH_3, etc.							
Methyl cyclohexanol	Sextol Hydrolin Methyl adronol Methylanol Methyl hexalin Heptalin Hexahydrocresol		114	160–180		0·925 (15° C.)	130 155	1·460	
Octyl alcohol		$CH_3(CH_2)_6CH_2OH$	130·1	194	−16	0·834 (20° C.)	178	1·4300	0·3 (20° C.) <1 (30° C.)
Propyl alcohol	Propanol	C_3H_7OH	60·1	97	−127	0·804 (20° C.)	67	1·386	
Propyl alcohol iso	Isopropanol Petrohol Solisol Avantine Persprit Losungmittel 8951		60·1	82	−86	0·791 (15° C.)	54 70	1·381	34 (20° C.) 60 (30° C.)
Propylene glycol 1 . 2			76·1	187		1·038 (20° C.)	210	1·432	0·1 (20° C.)
Polyglycol				230–250		1·114 (20° C.) 1·116 (20° C.)	271		
Tetrahydrofurfuryl alcohol			102	177		1·051 (20° C.)		1·4508	<1 (30° C.)
Triethylene glycol		$(CH_2OCH_2CH_2OH)_2$	150·1	288	−5	1·125 (20° C.)	331		$<0·1$ (20° C.)

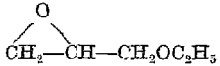
CONSTANTS OF SOLVENTS AND DILUENTS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (°C.).	M.Pt. (°C.).	S.G.	Flash Point (°F.).	R.I.	Vapour Pressure (mm.).
BENZOATES									
Ethyl benzoate		$C_6H_5COOC_2H_5$	150·1	213	−34	1·066 (0° C.)		1·505	
Methyl benzoate	Oil of Niobe	$C_6H_5COO . CH_3$	136·1	198		1·103 (0° C.)		1·516	
Propyl benzoate		$C_6H_5COOC_3H_7$	164·1	230	−52	1·025 (15° C.)			
Propyl benzoate iso		$C_6H_5COOCH(CH_3)_2$	164·1	218		1·023 (0° C.)			
BORATES									
Amyl borate		$(C_5H_{11})_3BO_3$	288	250–260		0·865		1·42	
Butyl borate		$(C_4H_9)_3BO_3$	245	190 (220 mm.)					
BUTYRATES									
Amyl *n*-butyrate iso		$CH_3CH_2CH_2COOCH_2CH_2CH(CH_3)_2$	158	178	−73	0·882 (0° C.)			
Butyl *n*-butyrate	Butol	$CH_3CH_2CH_2COOC_4H_9$	144	165	−91	0·888 (0° C.)	124	1·4049	4 (30° C.)
Butyl *n*-butyrate iso		$CH_3CH_2CH_2COOCH_2CH(CH_3)_2$	144	157		0·880 (0° C.)		1·4035	

Butyl isobutyrate iso		$(CH_3)_2CHCOOCH_2CH(CH_3)_2$	144	147	−81	0·875 (0° C.)	1·3999	
Ethyl *n*-butyrate		$CH_3CH_2CH_2COOC_2H_5$	116	120	−93	0·88 (20° C.) 0·900 (0° C.)	1·3932	22 (30° C.)
Ethyl isobutyrate		$(CH_3)_2CHCOOC_2H_5$	116	112	−88	0·890 (0° C.)	1·3903	
Ethyl hydroxy isobutyrate	Ethyl oxybutyrate	$(CH_3)_2C(OH)COOC_2H_5$	132	142–146		0·982 (20° C.)		
Methyl butyrate		$CH_3CH_2CH_2COOCH_3$	102	102	< −95	0·919 (0° C.)	1·3879	
Methyl isobutyrate		$(CH_3)_2CHCOOCH_3$	102	92	−85	0·911 (0° C.)	1·384	
Propyl *n*-butyrate		$CH_3CH_2CH_2COOC_3H_7$	130	143	−95	0·893 (0° C.)	1·4005	
Propyl *n*-butyrate iso		$CH_3CH_2CH_2COOCH(CH_3)_2$	130	128		0·879 (0° C.)		
CARBONATES								
Amyl carbonate iso		$((CH_3)_2CHCH_2CH_2)_2CO_3$	202·2	229		0·911	1·417	
Butyl carbonate		$(C_4H_9)_2CO_3$	174·1	207		0·928	1·412	
Butyl carbonate iso		$((CH_3)_2CHCH_2)_2CO_3$	174·1	190		0·919	1·407	

CONSTANTS OF SOLVENTS AND DILUENTS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (°C.).	M.Pt. (°C.).	S.G.	Flash Point (°F.).	R.I.	Vapour Pressure (mm.).
CARBONATES (*cont.*)									
Ethyl carbonate	Diatol Eufin	$(C_2H_5)_2CO_3$	118·1	126	−43	0·980	120	1·385	
Methyl carbonate		$(CH_3)_2CO_3$	90	90	0·5	1·076		1·369	
Propyl carbonate		$(C_3H_7)_2CO_3$	146·1	168		0·946		1·401	
Propyl carbonate iso		$\left(\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH\right)_2CO_3$	146·1	147		0·921		1·393	
ETHERS AND OXIDES									
Diamyl ether		$(C_5H_{11})_2O$	158	170–190		0·780 (21° C.)			
Anisole		$C_6H_5OCH_3$	108·1	154	−38	0·988 (21° C.)			
Benzyl Cellosolve		$C_6H_5CH_2OCH_2CH_2OH$	152	254–258		1·070 (20° C.)			<1 (30° C.)
Dibutyl ether		$(C_4H_9)_2O$	130·1	143		0·7713 (20° C.)	100		5 (20° C.)
Monobutyl ether of ethylene glycol	Butyl glycol Butyl Cellosolve	$C_4H_9OCH_2CH_2OH$	118·1	171		0·9017 (20° C.)	140 165	1·4177	0·9 (20° C.)
Monobutyl ether of diethylene glycol	Butyl Carbitol	$C_4H_9OCH_2CH_2OCH_2CH_2OH$	162·1	231		0·955 (20° C.)	230		<0·1 (20° C.)
1 . 4 . Diethylene dioxide	Dioxane	$O\!<\!\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}\!>\!O$	88·1	101·5	−12	1·035 (20° C.)	41 52 65	1·423	26 (20° C.)

22′ Dichlorethyl ether	Chlorex	$ClCH_2CH_2OCH_2CH_2Cl$	143	178·5	−50	1·222 (20° C.)	131 172	1·457	0·7 (20° C.)
Diethyl ether	Sulphuric ether	$(C_2H_5)_2O$	74·1	35		0·719 (15° C.)	<20	1·350	442 (20° C.)
Monoethyl ether of ethylene glycol	Cellosolve Solvulose	$C_2H_5OCH_2CH_2OH$	90·1	135		0·931 (20° C.)	104 111	1·408	4 (20° C.)
Diethyl ether of ethylene glycol		$C_2H_5OCH_2CH_2OC_2H_5$	118·1	121		0·853 (20° C.)		1·3914	
Monoethyl ether of diethylene glycol	Carbitol	$C_2H_5OCH_2CH_2OCH_2CH_2OH$	134·1	198 202		0·990 (20° C.)	200 210	1·43	<0·1 (20° C.)
Ethyl glycerol diether		$(CH_2OC_2H_5)_2CHOH$	148	191		0·952		1·419	
α-Ethyl glycerol monoether		$CH_2OHCHOHCH_2OC_2H_5$	120	222		1·063 (25° C.)		1·441	
Ethyl glycerol triether		$CH_2OC_2H_5CHOC_2H_5CH_2OC_2H_5$	176	181		0·886 (25° C.)		1·407	
Epiethylin or Glycidylethyl ether			102	124–126		0·94			
Epiphenylin or Glycidylphenyl ether			150	130–132 (22 mm.)		1·11			
α-Methyl glycerol monoether		$CH_3OCH_2CHOHCH_2OH$	106	220		1·11 (25° C.)			
α-β-Methyl glycerol diether		$CH_3OCH_2CH_3OCH\ .\ CH_2OH$	120	180		1·016 (25° C.)			
Methyl glycerol triether		$CH_3OCH_2CH_3OCH\ .\ CH_2OCH_3$	134	148		0·937 (25° C.)			
Monomethyl ether of ethylene glycol	Methyl glycol Methyl Cellosolve	$CH_3OCH_2CH_2OH$	76·1	124		0·966 (20° C.)	97 105	1·40	7 (20° C.)
Monomethyl ether of diethylene glycol	Methyl Carbitol	$CH_3OCH_2CH_2OCH_2CH_2OH$	120·1	193		1·035 (20° C.)	200		0·2 (20° C.)

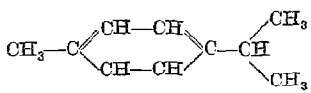
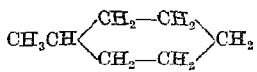
CONSTANTS OF SOLVENTS AND DILUENTS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (°C.).	M.Pt. (°C.).	S.G.	Flash Point (°F.).	R.I.	Vapour Pressure (mm.).
ETHERS AND OXIDES (*cont.*)									
Dipropyl ether		$(C_3H_7)_2O$	102·1	90·1		0·752			
Propyl ether iso		$(CH_3)_2CH\text{—}O\text{—}CH(CH_3)_2$	102·1	67·5		0·7258 (20° C.)	<20		158 (20° C.)
Propylene oxide		OCH_2CHCH_3	58	34		0·8313 (20° C.)	<20		395 (20° C.)
Glycerol monophenyl ether	Autodyne	$CH_2OHCHOHCH_2OC_6H_5$	168						
Propyl Cellosolve iso		$(CH_3)_2CHOCH_2CH_2OH$	104	140–143		0·906 (20° C.)			8 (30° C.)
FORMATES									
Amyl formate		$C_5H_{11}H\,.\,COO$	116	130	−73	0·893 (15° C.)	80	1·3951	
Amyl formate iso		$(CH_3)_2CHCH_2CH_2\,.\,H\,.\,COO$	116	124		0·871 (20° C.)		1·391	
Benzyl formate		$C_6H_5CH_2H\,.\,COO$	136	201		1·08 (20° C.)		1·519	
Butyl formate		$C_4H_9H\,.\,COO$	102	107	−90	0·911 (0° C.)		1·389	23
Butyl formate iso		$(CH_3)_2CHCH_2H\,.\,COO$	102	98	−95	0·875 (20° C.)		1·386	

Ethyl formate	Formosol	$C_2H_5H . COO$	74	54	−80	0·938 (0° C.)		1·306	
Methyl formate		$CH_3 . H . COO$	60	32	−99	0·999 (0° C.)			
Propyl formate		$C_3H_7 . HCOO$	88	81	−93	0·918 (0° C.)		1·377	
Propyl formate iso		$(CH_3)_2CH . H . COO$	88	68		0·883 (0° C.)			
FUROATES									
Amyl furoate iso		$C_5H_{11}COO . OC_4H_3$	182·1	233 136/25 mm.		1·0335 (20° C.)		1·472	
Butyl furoate		$C_4H_9COO . O . C_4H_3$	168·1	233 119/25 mm.		1·0555 (20° C.)		1·474	
Ethyl furoate		$C_2H_5COO . O . C_4H_3$	140·1	195/706 mm.	34	1·177 (20° C.)		1·4699	
Methyl furoate		$CH_3COO . O . C_4H_3$	126	181		1·1786 (20° C.)		1·4869	
Propyl furoate		$C_3H_7COO . O . C_4H_3$	154·1	211		1·0745 (20° C.)		1·475	
HYDROCARBONS									
	Benzine			55–155		0·739–0·743 (15° C.)	<40	1·38 1·44	
	Benzol (B.E.S.A. 3 D10.)			78–82 (95 %)		0·882 0·886	<73	1·50	
	Coml. 90 % benzol			90 % below 100° C.		0·86 (15° C.) 0·88 (15° C.)	−5	1·497	
Benzene		C_6H_6	78·1	80	5·5	0·8791 (20° C.)	<41 46	1·5012	118 (30° C.)
Cumene		$C_6H_5CH(CH_3)_2$	120	152		0·875 (4° C.)		1·506	

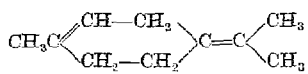
CONSTANTS OF SOLVENTS AND DILUENTS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (°C.).	M.Pt (°C.)	S.G.	Flash Point (°F.).	R.I.	Vapour Pressure (mm.).
HYDROCARBONS (*cont.*)									
Cyclohexane	Hexamethylene Hexahydrobenzene Naphthene	$CH_2<\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}>CH_2$	84·1	80	4	0·790 (20° C.)	<40	1·426 1·429	77 (20° C.)
	Creosote					1·03 1·04			
Decahydro-naphthalene	Decalin	$C_{10}H_{18}$	138	175–205 192		0·894 (20° C.)	135 145	1·467	2 (30° C.)
Dipentene		$C_{10}H_{16}$	136	176–198 181		0·850 (15° C.)	130	1·473 (20° C.)	2 (30° C.)
	Distillate			140–245		0·800–0·805 (15° C.)	94 115		
	Pool distillate			150–280		0·795 (15·5°C.)	104		
	Crude distillate					0·823–0·829 (15° C.)	>120		
Ethyl benzene		$C_6H_5C_2H_5$	*106*	*135*		0·872	59		
	Fuel oil					0·951–0·954			
	Hydroterpin			180–195		0·879 (20° C.)		1·4733	
	Hydrogenated naphtha. 1			95–137		0·793	48 60		
	Hydrogenated naphtha. 2			136–186		0·860	61 80		

	Hydrogenated naphtha. 3			186–216		0·890	135 140	
	Hydrogenated naphtha. 4			215–280		0·950	150 190	
p-Methyl isopropyl benzene	Cymene Cymol		134·2	175		0·860 0·872 (0° C.)	212	1·49
Mesitylene		$C_6H_3(CH_3)_3$	120·1	164		0·877 (4° C.)		
Methyl cyclohexane			98·1	101	−126	0·733 0·760		1·423
	Light solvent naphtha			105–165		0·865– 0·875 (15° C.)	70 73	
	Heavy naphtha			160–190		0·890– 0·900 (15° C.)	100 120	1·496
	Pine oil			212–218 120–225		0·93 (15° C.) 0·95 (15° C.)	176 185 200	1·480 1·483
	Petroleum ether			40–60		0·670 (15° C.)	<40	1·38
	Petrol No. 2 Petrol, aviation Petroleum benzol substitute			44–185 42–160 75–95		0·760 0·760 0·796	<73 <73	1·37 1·45
	Paraffin oil			155–275		0·805– 0·817 (15° C.)	120 130	
	Pool paraffin oil (kerosene)			160–285		0·800 (15·5° C.)	115	

CONSTANTS OF SOLVENTS AND DILUENTS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (°C.).	M.Pt. (°C.).	S.G.	Flash Point (°F.).	R.I.	Vapour Pressure (mm.).
HYDROCARBONS (*cont.*)									
	S.B.P. 1			35–115		0·675 0·695 (15·5° C.)	−54		3·2 lb./in.² (15·5° C.)
	S.B.P. 2			70–95		0·700 0·720 (15·5° C.)	−40		1·3 lb./in.² (15·5° C.)
	S.B.P. 3			100–120		0·735 0·755 (15·5° C.)	+15		0·3 lb./in.² (26·5° C.)
	S.B.P. 4			40–150		0·705 0·730 (15·5° C.)	−48		2·2 lb./in.² (15·5° C.)
	S.B.P. 5			90–105		0·725 0·745 (15·5° C.)	−7		0·8 lb./in.² (26·5° C.)
	S.B.P. 6			140–160		0·770 0·790 (15·5° C.)	+74		0·6 lb./in.² (38° C.)
	R.S. (rubber solvent)			100–160		0·745 0·770 (15·5° C.)	+40		0·3 lb./in.² (26·5° C.)

	Rosin spirit Pinolin			150–300	0·890 0·930	97 102	1·48 1·50	
	770 spirit			100–150	0·750– 0·760 (15° C.)	<73		
	White spirit B.E.S.A. Spec. × 20			min. 80 % below 190° C. min. 90 % below 200° C.	0·800 max.	90–100 usually 75 (min.)	1·38 1·41	
	Pool white spirit			149–195	0·801 (15·5° C.)	94		0·15 [2] lb./in. (38° C.)
	Shale oil			65–100	0·718 0·730 0·773	60 70		
	Solvenol			165–212	0·850 (15° C.) 0·866 (15° C.)		1·470 1·478	
	Terpinolene		136	98–225 185	0·855	111	1·4823	
Tetrahydro-naphthalene	Tetralin Tetranap	$C_{10}H_{12}$	132	198–210 206	0·971 (20° C.)	170 172 180	1·540	<1 (30° C.)
	Turpentine Type I American gum, B.S.S. 1936			94 % between 150–170	0·862 (15° C.) 0·872 (15° C.)	90 95	1·469 1·478	
	Turpentine Type II Wood turps, B.S.S. 1936			at least 69 % below 170° C. and 89 % below 180° C.	0·859 (15° C.) 0·875 (15° C.)	90 97	1·463 1·483	
	Toluol (coml.)			105–112	0·868	45 55	1·495	

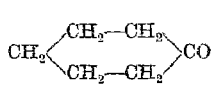
CONSTANTS OF SOLVENTS AND DILUENTS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (°C.).	M.Pt. (°C.).	S.G.	Flash Point (°F.).	R.I.	Vapour Pressure (mm.).
HYDROCARBONS (*cont.*)									
	Toluol DTD 112			95 % between 109–111		0·868 0·871			
Toluene		$C_6H_5CH_3$	92·1	110	−97	0·871 (13° C.)	45	1·496	26 (30° C.)
	Tar spirit			120–270		0·975–1·025 (15° C.)	90 110	1·481	
	Toluol substitute (45–50 % aromatics)			100–120		0·800			
	T.V.O. vaporising oil (40–50 % aromatics)			140–270		0·831–0·834	97 101		
	Pool vaporising oil			145–265		0·830 (15·5° C.)	95		
	Xylol substitute			140–160		0·805	76		
	Coml. xylol (mixture of isomers)			90 % between 135–145		0·864	75 80	1·497 1·500	
Xylene		$C_6H_4(CH_3)_2$	106·1	138–140			85		
HALOGENATED COMPOUNDS									
Amyl chloride		$C_5H_{11}Cl$	106·6	105–109		0·883 (20° C.)			
Butyl chloride		C_4H_9Cl	92·6	77	−123	0·887 (20° C.)			

Butyl chloride iso		$(CH_3)_2CHCH_2Cl$	92·6	68	−131	0·875		1·3960	
Butyl chloride tert.		$(CH_3)_3CCl$	92·6	51	−28	0·847 (15° C.)		1·3869	
Benzyl chloride		$C_6H_5CH_2Cl$	126·6	179	−41	1·114		1·5415	
Carbon tetrachloride	Asordin Tetraform Tetrakol Tetra Benzinoform Phoenixine Spectrol Katarin	CCl_4	154	78	−24	1·608 (10° C.)	non-inflam.	1·460	91 (20 mm.)
Chloroform		$CHCl_3$	119·5	61		1·504 (12° C.)	non-inflam.	1·445 1·449	162
Dichlorethylene sym.	Losungmittel THD	$CHCl \parallel CHCl$	97	55		1·25	52	1·505	205 (20° C.)
Dichlorhydrine		$ClCH_2CH(OH)CH_2Cl$	128	174 176		1·36	165	1·47	7
Dichlorethyl ether sym. α . α'		$CH_3CHClOCHClCH_3$	143	116		1·137 (12° C.)		1·457	
Dichlorethyl ether sym. β . β'		$(ClC_2H_4)_2O$	143	177	−52	1·213	131 172	1·457	0·7 (20° C.)
Dichlorbenzene meta		$C_6H_4Cl_2$	147	172	−18	1·307 (0° C.)			
Dichlorbenzene ortho	Orthene	$C_6H_4Cl_2$	147	179	−14	1·327 (0° C.)	120	1·5489	
Dichlorbenzene para		$C_6H_4Cl_2$	147	172	53				
Ethylene chlorhydrin		CH_2OH $\vert$ CH_2Cl	80·5	129	−69	1·203	131 140	1·444 (15° C.)	6 (20°C.)

CONSTANTS OF SOLVENTS AND DILUENTS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (°C.).	M.Pt. (°C.).	S.G.	Flash Point (°F.).	R.I.	Vapour Pressure (mm.)
HALOGENATED COMPOUNDS (*cont.*)									
Ethylene dichloride (sym. dichlorethane)		CH_2Cl | CH_2Cl	99	83 80–86	−35	1·252 (20° C.)	54 63	1·444 (20° C.)	65 (20° C.)
Epichlorhydrine		$CH_2—CH—CH_2Cl$ $\diagdown O \diagup$	92	117	−48	1·19		1·438	
Monochlorbenzene	Chlorbenzol Puran	C_6H_5Cl	112·5	132	−40	1·113	83	1·525	9 (20° C.)
Monochlorhydrin		$ClCH_2CH(OH)CH_2OH$	110·5	213–228 (decomp.)		1·28 1·35			
Methylene chloride	Solaesthin Losungmittel LWH	CH_2Cl_2	85	40 42		1·328 (15° C.) 1·346	non-inflam.	1·4235	147 (0° C.) 230 (10° C.)
Propyl chloride		$CH_3CH_2CH_2Cl$	78·5	46		0·891 (18° C.)			
Propyl chloride iso		$CH_3 \diagdown CHCl$ $CH_3 \diagup$	78·5	37	−117	0·859 (20° C.)			
Propylene chlorhydrin		CH_3CHOH | CH_2Cl	94·5	127		1·116	125		4 (20° C.)
Propylene dichloride		CH_3CHCl | CH_2Cl	113	96		1·159 (20° C.)	70		38 (20° C.)

Perchlorethylene	Tetralex Eteline Perawin	CCl_2 ‖ CCl_2	166	121		1·631 (9° C.)		1·502 1·506	15 (20° C.)
Pentachlorethane	Pentaline	$CHCl_2$ | CCl_3	202·5	161		1·68 1·70	non-inflam.	1·5035	5 (20° C.)
Trichlorethane α and β		CH_2Cl | $CHCl_2$	133·5	114		1·457 (10° C.)			
Tetrachlorethane sym.	Alanol Westron Emaillet Tetraline Novania	$CHCl_2$ | $CHCl_2$	168	147		1·614 (0° C.)	non-inflam.	1·495	11 (20° C.)
Trichlorethylene	Chlorylen Comedol Westrosol Drawin CH Trieline Tri	$CHCl$ ‖ CCl_2	131·5	88		1·471 1·479	non-inflam.	1·478	56 (20° C.)
KETONES									
Acetonyl acetone		$CH_3COCH_2CH_2COCH_3$	114·1	188–193	−9	0·973		1·449	<2 (30° C.)
Acetophenone, (Phenyl methyl ketone)	Mittel HNA Acetyl benzene	$CH_3COC_6H_5$	120	202	20	1·023 (25° C.)	105	1·536	
	Acetone oils	White acetone oil Yellow acetone oil		70–120 120–150					
Butyl ketone di-iso		$(CH_3)_2CHCH_2COCH_2CH(CH_3)_2$	142·1	164–169		0·808 (20° C.)			4 (30° C.)
Cyclohexanone	Sextone Hexanone Anon		98	154–156	−45	0·945	117 148	1·443 1·451	7 (30° C.)

CONSTANTS OF SOLVENTS AND DILUENTS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (°C.).	M.Pt. (°C.).	S.G.	Flash Point (°F.).	R.I.	Vapour Pressure (mm.).
KETONES (*cont.*)									
Diacetone alcohol	Dial Pyranton A Losungmittel DA	$\begin{matrix}CH_2\\CH_3\end{matrix}\!\!>\!C(OH)CH_2COCH_3$	116	164	−55	0·942	95 122	1·4204	9 (20° C.)
Diethyl ketone		$C_2H_5COC_2H_5$	86	102	−42	0·834 (0° C.)		1·3927	46 (30° C.)
Dimethyl ketone	Acetone	CH_3COCH_3	58	56	−95	0·7912 (20° C.)	<20 2	1·360	180 (20° C.)
Methyl ethyl ketone	M.E.K. Butanone	$CH_3COC_2H_5$	72	80	−86	0·830 (0° C.)	<32 19	1·379	77 (20° C.) 119 (30° C.)
	Methyl acetone B.E.S.A. 2 DI			50–70		0·830	<32		
Mesityl oxide		$CH_3COCH{=}C(CH_3)_2$	98	130	−59	0·858 (20° C.)	78	1·4439	<10 (30° C.)
Methyl cyclohexanone	Sextone B Methyl anon	$C_7H_{12}O$	112	160–170		0·925	118 130	1·44 1·45	4 (30° C.)
Methyl isobutyl ketone	Hexone	$(CH_3)_2CHCH_2COCH_3$	100·1	118	−85	0·802 (20° C.)	74	1·3959	13 (20° C.)
Methyl butyl ketone	Hexanone 2	$CH_3COC_4H_9$	100·1	114–137	−57	0·818	73	1·4024	10 (20° C.) 17 (30° C.)
Methyl amyl ketone	Heptanone 2	$CH_3COC_5H_{11}$	114·1	147–153		0·818	106	1·4110	4 (20° C.) 7 (30° C.)

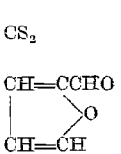
Methyl hexyl ketone		$CH_3COC_6H_{13}$	128	169–173	−22	0·820 (20° C.)		1·4161	3 (30° C.)
Phorone		$(CH_3)_2{=}C{=}CHCOCH{=}C{=}(CH_3)_2$	138·1	197–200	28	0·8850 (20° C.)		1·4998	<1 (30° C.)
Pinacoline		$CH_3COC(CH_3)_3$	100	106		0·800 (16° C.) 0·826 (0° C.)			
Dipropyl ketone	Butyrone	$C_3H_7COC_3H_7$	114·1	143	−33	0·8162 (20° C.)	120	1·4072 (20° C.)	5 (20° C.)
LACTATES									
Amyl lactate		$CH_3CH(OH)COOC_5H_{11}$	160	210		0·968 0·972			
Butyl lactate	Butacol	$CH_3CH(OH)COOC_4H_9$	146	185–195	−43	0·986	143		5 (30° C.)
Butyl lactate sec.		$CH_3CH(OH)COOCH(CH_2CH_3)(CH_3)$	146	172		0·972			
Butyl lactate iso		$CH_3CH(OH)COOCH_2CH(CH_3)_2$	146	168–200		0·976			
Ethy. lactate	Lembitol Acytol Eusolvan Normanol Solactol Acetylol Estisol	$CH_3CH(OH)COOC_2H_5$	118	154		1·024 (20° C.) 1·036	110 117	1·4111	5 (30° C.)
Methyl lactate		$CH_3CH(OH)COOCH_3$	104	145		1·090 (15° C.)	100	1·4156	
Propyl lactate		$CH_3CH(OH)COOC_3H_7$	132						
Propyl lactate iso		$CH_3CH(OH)COOCH(CH_3)_2$	132·1	155–165		0·988 (30° C.)			5 (30° C.)

CONSTANTS OF SOLVENTS AND DILUENTS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (°C.).	M.Pt. (°C.).	S.G.	Flash Point (°F.).	R.I.	Vapour Pressure (mm.)
NITRO COMPOUNDS									
Nitromethane		CH_3NO_2	61·0	101	−29	1·139 (20° C.)	112 (open cup)	1·3818	27·8 (20° C.)
Nitroethane		$CH_3CH_2NO_2$	75·1	114	−90	1·052 (20° C.)	106 (open cup)	1·3916	15·6 (20° C.)
1-Nitropropane		$CH_3CH_2CH_2NO_2$	89·1	132	−108	1·003 (20° C.)	120 (open cup)	1·4015	7·5 (20° C.)
2-Nitropropane		$CH_3CHNO_2CH_3$	89·1	120	−93	0·992 (20° C.)	103 (open cup)	1·3941	12·9 (20° C.)
1-Chloro 1-nitroethane		$CH_3CH(NO_2)Cl$	109·5	122–128·5 (90%)		1·258 (20° C.)	133 (open cup)	1·423	
1-Chloro 1-nitropropane		$CH_3CH_2CH(NO_2)Cl$	123·5	139–143 (90%)		1·209 (20° C.)	144 (open cup)	1·430	
2-Chloro-2-nitropropane		$CH_3C(NO_2)Cl\,CH_3$	123·5	129–132 (90%)		1·193 (20° C.)	135 (open cup)	1·425	
1, 1-Dichloro-1 nitroethane		$CH_3C(NO_2)Cl_2$	144	122–125 (90%)		1·405 (20° C.)	168 (open cup)	1·441	
1, 1-Dichloro-1 nitropropane		$CH_3CH_2C(NO_2)Cl_2$	158	141–144 (90%)		1·314 (20° C.)	151 (open cup)	1·443	

OXALATES								
Diamyl oxalate		$COOC_5H_{11}$ | $COOC_5H_{11}$	230	265		0·97	240	
Dibutyl oxalate	Losungmittel O Mittel OC	$COOC_4H_9$ | $COOC_4H_9$	202	243		1·001 (0° C.)	212	1·425
Dibutyl oxalate iso		$COOCH_2CH(CH_3)_2$ | $COOCH_2CH(CH_3)_2$	202	229		1·002 (14° C.)		
Diethyl oxalate		$COOC_2H_5$ | $COOC_2H_5$	146	185	−40	1·085	168	1·410
Dimethyl oxalate		$COOCH_3$ | $COOCH_3$	118	163	54	1·422		1·379
Dipropyl oxalate		$COOC_3H_7$ | $COOC_3H_7$	174	213		1·038 (0° C.)		
Dipropyl oxalate iso		$COOCH(CH_3)_2$ | $COOCH(CH_3)_2$	174	190		1·010 (18° C.)		
PROPIONATES								
Amyl propionate		$CH_3CH_2COOC_5H_{11}$	144	140–170 165	−73	0·871	105	
Amyl propionate iso		$CH_3CH_2COOCH_2CH_2CH(CH_3)_2$	144	160		0·888 (0° C.)		1·4065

CONSTANTS OF SOLVENTS AND DILUENTS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (°C.).	M.Pt. (°C.).	S.G.	Flash Point (°F.).	R.I.	Vapour Pressure (mm.)
PROPIONATES (*cont.*)									
Butyl propionate	Losungmittel BP	$CH_3CH_2COOC_4H_9$	130	146	−90	0·895 (0° C.)	113	1·3982	7 (30° C.)
Butyl propionate iso		$CH_3CH_2COOCH_2CH(CH_3)_2$	130	137	−71	0·888 (0° C.)			
Ethyl propionate	Ester P	$CH_3CH_2COOC_2H_5$	102	98	−73	0·912 (0° C.)	60	1·3844	43 (30° C.)
Methyl propionate		$CH_3CH_2COOCH_3$	88	79	−88	0·937 (0° C.)		1·3776	
Propyl propionate		$CH_3CH_2COOC_3H_7$	116	122	−76	0·902 (0° C.)		1·3935	
Propyl propionate iso		$CH_3CH_2COOCH(CH_3)_2$	116	111		0·893 (0° C.)			
VARIOUS									
Carbon disulphide		CS_2	76·1	46	−112	1·272	−17 −4	1·635	
Furfural			96	161		1·159 (20° C.)	133 >200	1·5261	
Satd. methyl ester of abietic acid	Hercolyn			365–370		1·026	387	1·5177	

CHAPTER 9

PLASTICISERS

It is not only cellulose esters which require plasticisers but many other substances as well. Plasticisers are needed for spirit varnishes based on shellac or Manila, for chlorinated rubber, and for urea formaldehyde, phenol formaldehyde, vinyl, styrene, acrylic and alkyd resins. Plasticisation of these substances is not generally difficult except in the case of thermosetting phenol formaldehyde resins. The addition of ordinary plasticisers to these resins results in the complete breakdown of the normal thermosetting process. Plasticisation is effected, in these cases, by introducing plasticising agents to the other resin components at the time of the initial reaction. They may be in true combination ultimately. Drying oils, castor oil and glycerine are examples of such plasticisers.

Types of Plasticisers

Plasticisers cover a very wide range of different types of chemical compound. They include probably more types than are found among the volatile solvents. By far the most important group is that of the esters. Among the esters are acetates, propionates, butyrates, palmitates, stearates, oleates, laurates, adipates, citrates, oxalates, tartrates, succinates, sebacates, acrylates, abietates, ricinoleates, acetyl ricinoleates, glycollates, glycerides, benzoates, phthalates, hydrophthalates, salicylates, *o* and *p*-toluene sulphonates, lævulinates and phosphates. Other plasticisers are found among hydrocarbons, chlorinated hydrocarbons, alcohols, glycols, phenols, ketones, ethers, toluenesulphonamides, acetanilides, oxanilides, sulphanilides, thiocarbanilides and naphthanilides. Natural plasticisers or plasticisers which are not synthesised by chemical reactions, include the vegetable oils, pine oils, gum elemi, gum thus and Venice turpentine. Blown vegetable oils are also popular for certain purposes.

In assessing the suitability of a plasticiser for a given purpose, the following factors should be considered.

Boiling Range

A rough guide to the suitability of a substance for use as a plasticiser is given by its boiling range. Jordan states that the most satisfactory plasticisers boil above 250° C. at ordinary pressure.[1]

Compatibility

The main function of a plasticiser is to confer flexibility on a film, and this should be accomplished without sacrificing other essential film properties, such as adhesion or film strength. These properties are

dependent on the degree of compatibility or miscibility of the plasticiser with the other film components. The tensile strengths of films vary considerably, both with amount and type of plasticiser used. According to Ivanova and Rogovin the effect of plasticisers alters with their position in the homologous series. The lower members may cause a reduction in strength of film, but higher members give improved strength in proportion to their molecular weights.[2]

The plasticiser should be miscible in all proportions with the resin or compound requiring plasticising. The criteria for complete miscibility are clarity and non-sweating. The mixture should be clear whether the solvent is present or not. In other words, the ultimate dried film should be quite bright and free from precipitation or opalescence. Some substances are not true plasticisers in that they tend to sweat out from films gradually on ageing. Whilst they are not satisfactory for all purposes, such plasticisers do cause softening of films and they have a certain utility. The sweating out of plasticisers can be prevented by incorporating with them the necessary amount of true solvent plasticiser. The best plasticisers are miscible with the other film components in all proportions. Although the amount of plasticiser present is, in most cases, substantially less than that of the other components, miscibility in all proportions minimises the chances of failure, and helps to accommodate any loss of compatibility consequent upon lowering of temperature. Reduction of compatibility with decrease in temperature should be examined for by comparing the flexibilities obtained with different plasticisers at low temperatures. Plasticisers exhibiting the most pronounced brittleness under these conditions should be eliminated. Plasticisers which are solid at ordinary temperatures should be examined for tendency to crystallise at lower temperatures.

The general compatibility of plasticisers and their volatility, diminish with increasing molecular weight, especially in homologous series. Another factor to consider is the possible variation of compatibility with age of the film. Plasticisers such as vegetable oils which oxidise on exposure may tend to become incompatible in the oxidised condition. In certain classes of lacquer, the plasticising property of vegetable oils diminishes with the susceptibility of the oils to oxidation.[3]

Solvent Power

Plasticisers may be regarded as good solvents. With solvents of exceptionally good solvent power it is possible to add controlled amounts of cheaper diluents. A similar procedure is possible with good plasticisers. In a composition comprising a plasticiser, a base resin, and a cheap resin, the two resins may not be completely miscible alone. In this case the presence of plasticiser may permit a homogeneous mixture to be made.

The addition of plasticiser, which is tantamount to adding a strong solvent, will result in a reduction of viscosity of the lacquer. Since many plasticisers are esters, of which a characteristic property is outstanding

solvent power, a small amount often produces a considerable reduction in viscosity. Mixtures of plasticisers with other solvents may be especially effective in this respect. With the same argument that plasticisers may be regarded as good solvents, cheaper diluents may be added judiciously to solvent mixtures. Since plasticisers have low vapour pressures, it is unnecessary to consider the effect on the non-volatile constituents of film, of the evaporation of the volatile constituents. When these disappear the resultant film is clear and homogeneous, because the plasticiser is chosen specifically to yield this condition.

Stability

For permanent plasticising effect under conditions of normal exposure the plasticiser should be inert to atmospheric influences. The ideal to be aimed at is complete stability to the action of light, oxygen and moisture, or to the combined effect of these influences. Disintegration is revealed as darkening of the film, or hydrolysis of the plasticiser may occur.

In compositions subjected to elevated temperatures, either during initial stoving or subsequently, the decomposition of the plasticiser may become more pronounced. If, during the life of a plasticised film its average temperature is substantially higher than normal atmospheric temperature, for example, on radiators, the effect of the aforementioned atmospheric influences may be greatly stimulated. Where films are required for use at very high temperatures the plasticiser must be examined for resistance to carbonisation.

In assessing plasticisers for resistance to darkening under the action of light, Jordan advocates conducting tests in the presence of other constituents, because of the fact that plasticisers often absorb a wider range of light waves than the other constituents of the film.[4]

Some ester plasticisers are readily hydrolised by the action of water, and this tendency should be tested. Tartrates, oxalates, triacetin, amyl borate, and ethyl *p*-toluene sulphonate, are plasticisers which tend to split off free acid in the presence of water. Plasticisers should exhibit no increase in free acidity after boiling with water.

Permanent plasticity is only obtained with plasticisers of low vapour pressures. This can be examined for by some of the methods used for the determination of evaporation rates of solvents. Thus small amounts of plasticiser can be exposed in flat trays, and the loss by evaporation computed at convenient intervals of time. By comparison with solvents, the test with plasticisers is, if necessary, much more prolonged. Whereas with the former, the test occupies up to a few hours only, good plasticisers may require several days' exposure before any measurable loss occurs. In assessing the evaporation rate of plasticisers, some workers prefer to hasten the process by conducting the determination at elevated temperatures. Temperatures in the range, 50°–100° C., have been used. There is, however, a certain artificiality about the choice of such temperatures which would be rarely encountered in practice. On the other hand,

however, where plasticisers are incorporated in compositions subjected to stoving, it is of paramount importance that the volatilities at the stoving temperature are determined. Using nitrocellulose as the foundation of a film, Kraus has concluded from experimental results that after seven days at 100° C., diphenyl, dilauryl and dicetyl phthalates, dicetyl hydrophthalate, tricresyl phosphate and Sipalin MOM may be regarded as practically non-volatile.[5] The evaporation rate of plasticisers is reduced in mixtures due to the presence of other components.

Chemical Resistance

Coating compositions are sometimes required for special purposes, where resistance to acid, alkali, solvents, water or combustion is essential. The choice of plasticiser will be governed by these considerations.

Data relating to the alkali resistance of plasticisers has been provided by Van Houckeroth.[6]

Water Resistance

Where the water resistance of a film is of primary importance, plasticisers should be selected which are non-hygroscopic and which show no tendency to dissolve in water. The tendency of a plasticiser to dissolve in water can be determined readily by shaking it up with water, and estimating the amount which goes into the aqueous layer. It is sometimes deemed preferable to ascertain water solubility by steeping the dried film in water for a specified time, allowing the film to dry out, and estimating the loss in weight. This loss may be regarded as plasticiser, on the assumption that the other film components are insoluble in water. This method has the advantage that it provides a film for visual examination which has been exposed to the influence of water immersion. Similar methods may be used for ascertaining resistance of plasticised films to other solvents such as alcohol and petrol. Triacetin is a typical plasticiser exhibiting inferior water resistance. The commercial ester contains both mono and diacetins which are soluble in water. A similar ester based on butyric acid (tributyrin) is less soluble in water than triacetin. Films containing tributyl phosphate, triamyl citrate, or the acetate ester of oleyl alcohol are practically unaffected after fourteen days' immersion in water.[5] Water solubility tests conducted on plasticisers at 25° C. by Trimmer, show castor oil and tricresyl phosphate to have negligible solubility, followed by dibutyl and diamyl phthalates, diethyl phthalate and camphor. Dibutyl tartrate exhibits a substantially greater solubility than any of the foregoing, with triacetin the most soluble of all.[7]

Petrol Resistance

Plasticisers with good petrol resistance are the toluene sulphonamides, glyceryl tribenzoate, dimethyl phthalate, diethyl glycol phthalate, Plassitil and hydroxynaphthanilide 2 . 3.

Irregularities of Solvency

Irregularities of solvency may occur when plasticisers are incorporated in films. Where there is a possibility of chemical affinity between the plasticiser and the other component the solubility of the plasticiser may be diminished. The plasticisation of nitrocellulose with castor oil is an example of this phenomenon. If such films are subjected to the action of heat and sunlight to facilitate drying, subsequent attempts to estimate plasticiser by extraction yield unreliable results.[8] Under certain conditions, therefore, films of improved solvent resistance can be obtained by exploiting this phenomenon.

Non-inflammability

For non-inflammable compositions such as those required for cable dopes, incombustible plasticisers must be chosen. The most popular non-inflammable plasticisers are, tricresyl phosphate, triphenyl phosphate, amyl borate, organic silicates, polyglycerol acetate, dichloroethyl phosphate and chlorinated diphenyls.

Colour and Clarity

Plasticisers should be examined for colour especially when they are used in pale lacquers or in media which will be pigmented with white pigments. They should be clear and free from suspended matter, for the presence of suspended matter detracts from the gloss of the resultant film and causes other imperfections.

Odour

The odour of plasticisers is even more important than the odour of volatile solvents. Whereas with the latter an objectionable smell is present during application only, with plasticisers it persists indefinitely. It is readily appreciated that in certain circumstances, such as in lacquers for food containers, the presence of a strongly smelling plasticiser could not be tolerated. However, a plasticiser with a slight but pleasant odour can be used to mask the smell of other constituents.

Toxicity

It is not so important to consider plasticisers for toxicity as it is with solvents. Because of their low vapour pressures there is very little risk of poisoning by inhalation with plasticisers. The chief risk is of absorption through the skin, with the remote possibility of absorption through the mouth. Published information on the toxicity of plasticisers is scanty. If *o*-tricresyl phosphate is taken internally or absorbed through the skin, it exerts a paralytic action which is absent with the meta and para isomers. Camphor, which at one time enjoyed a wide popularity as a cellulose plasticiser, is rather more toxic than is generally realised. Small doses produce a stimulating effect only, but larger doses paralyse

the respiratory and central nervous systems besides interfering with the action of the heart. The toxic effect of pine oils is said to be more pronounced than that of turpentine.

Catalytic Action

A special property of plasticisers is their possible catalytic effect upon thermosetting resins. Ester plasticisers, which on heating decompose slightly with evolution of free acid, may act catalytically upon the thermal polymerisation of urea formaldehyde resins.

Cost

Complex plasticisers which are synthesised from simple raw materials are often expensive. The choice of plasticiser is often controlled, therefore, by cost. In considering cost it should be remembered that the plasticising effect of plasticisers varies, and that a smaller amount of expensive plasticiser often gives the same or better result than a much larger amount of an inexpensive one.

Other Factors

Another effect of plasticisers on films is of aiding flow. They may also minimise solvent retention of films by assisting in the volatilisation of the quickly evaporating components. Plasticisers often result in a reduction in the temperature necessary for complete thermo-plasticity.

Addition of plasticiser has an influence on the gloss of the resultant film and the degree of gloss may vary with the amount present.

Some plasticisers are effective in minimising the blushing of films.

The durability of films to normal exposure is governed to a great extent by the type of plasticiser present. Variation in molecular structure produces variable durability.

Incorporation of Plasticisers

The method of incorporation of the plasticiser into the composition varies. It may be added directly to the other components before or after their solution.

A method of incorporating plasticiser in which the original physical state of the compound to be plasticised is unaltered, by avoiding mechanical working, consists in distributing the plasticiser over the compound and adding a non-solvent for the compound. The non-solvent is subsequently removed by evaporation.

Plasticisers which are normally solid can be dissolved in volatile solvents and incorporated in this way.[9]

Because of their low evaporation rates and convenient viscosities, plasticisers make admirable grinding media. In selecting a plasticiser for this purpose, other properties such as wettability and absorption by the pigment must be considered. Plasticiser absorption of pigments may be determined by the same methods as used for oil absorption. Buser

has observed a parallel with oil absorption figures,[10] but Van Heuckeroth points out that plasticiser absorption figures are higher than oil absorption figures.[11] When the pigment has been finely ground in the plasticiser over a roller mill, the paste is dispersed in the solution of the other ingredients.

Uses

Apart from improving the flexibility and adhesion of films plasticisers are used to reduce chalking, to act as fluxes during the dehydration of metallic soaps, for producing non-drying films such as are required for adhesives, and in paint removers where they perform the rôle of a non-volatile softening agent.

Recommendations for plasticisers for use with the various types of natural and synthetic resins, or chlorinated rubber, are given in the chapters devoted to these materials.

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CONSTANTS OF PLASTICISERS

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (° C.).	M.Pt. (° C.).	S.G.	Flash-Pt. (° F.).	R.I.
ABIETATES								
Benzyl abietate	Benzyl resinate Resin ether Plastolin I	$C_{19}H_{29}COOCH_2C_6H_5$	392			1·04		1·55
Ethyl abietate		$C_{19}H_{29}COOC_2H_5$	330	350	−45	1·03	329 352	1·52
Glyceryl diaceto abietate	Plastabrac AA							
Methyl abietate	Abalyn	$C_{19}H_{29}COOCH_3$	316	360–370		1·038	374	1·5297
ACETATES								
Benzyl acetate	Plastolin I	$C_6H_5CH_2OOCCH_3$	150·1	215	−51	1·061	202	1·5232
Bornyl acetate		$C_{10}H_{17}OOCCH_3$	196	96/11 mm. 223	29	0·991		1·4663
Diglyceryl ether tetra-acetate	Glyakol Glyacol	CH_2OOCCH_3 | $CHOOCCH_3$ | CH_2OCH_2 | $CH_3COO . CH$ | CH_3COOCH_2	334					
Glyceryl monocresyl ether diacetate	Abracol 777	$CH_2OC_6H_4CH_3$ | $CHOOC . CH_3$ | $CH_2OOC . CH_3$	266	310		1·35		1·49

Glyceryl dicresyl ether acetate	Abracol 888	$CH_2OC_6H_4CH_3$ | $CHOOCCH_3$ | $CH_2OC_6H_4CH_3$	314	360		1·115		1·53
Glyceryl triacetate	Triacetin	CH_2OOCCH_3 | $CHOOCCH_3$ | CH_2OOCCH_3	218	258	−78	1·161 (15° C.)	270	1·433
Glyceryl diacetate	Diacetin	CH_2OOCCH_3 | $CHOH$ | CH_2OOCCH_3	176	176/40 mm. 260	40	1·176 (15° C.)	295	1·44
Glyceryl mono-acetate	Monoacetin	CH_2OOCCH_3 | $CHOH$ | CH_2OH	134	158/165 mm.		1·218		1·5021
Glyceryl lactate triacetate	Plassitil			>200/5 mm.		1·2		
Resorcinyl diacetate		$C_6H_4(CH_3COO)_2$	194	278		1·19	293	1·507
Triethylene glycol diacetate				300	<−60	1·111		
ACETYL RICINOLEATES								
Butyl acetyl ricinoleate	Plasticiser P6 Baker's P6 RBA	$C_{17}H_{32}(OCOCH_3)COOC_4H_9$	397	400		0·930	230	1·457
Ethyl acetyl ricinoleate	Baker's P5 REA	$C_{17}H_{32}(OCOCH_3)COOC_2H_5$	369	400		0·931		1·456
ADIPATES								
Butyl adipate		$COOC_4H_9$ $(CH_2)_4$ $COOC_4H_9$	258	183/14 mm.	−37	0·965		

CONSTANTS OF PLASTICISERS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (° C.).	M.Pt. (° C.).	S.G.	Flash-Pt. (°F.).	R.I.
ADIPATES (*cont.*)								
Dicyclohexyl adipate	Sipalin AOC	$(CH_2)_4(COOC_6H_{11})_2$	310	212/12 mm.		1·030		
Ethyl adipate		$(CH_2)_4(COOC_2H_5)_2$	202	239	−21	1·009		
Dimethyl cyclohexyl β-methyl adipate	Sipalin MOM			216–224 12 mm.		1·009		1·468
Dimethyl cyclohexyl adipate	Sipalin AOM	$(CH_2CH_2COOC_6H_{10}CH_3)_2$	338	226–232 12 mm.		1·011		1·469
Diethoxy ethyl adipate		$C_2H_5OC_2H_4OCO(CH_2)_4COOC_2H_4OC_2H_5$	290		< −70	1·036		1·439
Dimethoxy ethyl adipate		$CH_3OC_2H_4OCO(CH_2)_4COOC_2H_4OCH_3$	262		−16	1·075		1·439
ALCOHOLS								
Benzyl alcohol	Plastoform I	$C_6H_5CH_2OH$	108·1	205	−15	1·050	205	1·5396
Pentaerythritol		$C(CH_2OH)_4$	136·1		253			1·550
Phenyl ethyl alcohol	Plastoform II	$C_6H_5CH_2CH_2OH$	122·1	220		1·024		
AMIDES								
Acetamide		CH_3CONH_2	59	222	81	1·156		

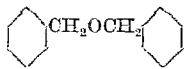
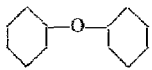
Cyclohexyl *p*-toluene sulphonamide	Santicizer IH				86		
Methyl *p*-toluene sulphonamide					78		
p-Toluene sulphonamide	Cellusol Abracol 789 Neu Camphrosal Santicizer I	CH_3 SO_2NH_2	171		137		
ANILIDES							
Acetanilide	Mittel ADT Phenyl acetamide	$NHCOCH_3$	135·1	304	115	1·21	329
Ethyl acetanilide	Mannol	$N(C_2H_5)COCH_3$	163	258	54	1·086	255
Formanilide		NHCHO	121	271	47	1·14	329
Hydroxy naphthanilide 2 . 3	Mittel PH Naphthol AIS				242		
Methyl acetanilide	Exalgen	$N(CH_3)COCH_3$	149	254	101		
Oxanilide	Camphol	NHCOCONH	240	320	245		
p-Toluene sulphanilide	Mittel PI Abracol 203	CH_3 $SO_2C_6H_4 . NH_2$	247		103		

CONSTANTS OF PLASTICISERS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (° C.).	M.Pt. (° C.).	S.G.	Flash-Pt. (° F.).	R.I.
ANILIDES (*cont.*)								
p-Toluene methyl sulphanilide	Mittel PO	CH_3 $SO_2C_6H_4N(CH_3)$	261		93			
Thiocarbanilide		$NHCSNH$	228	decomp.	153	1·321		
BENZOATES								
Amyl benzoate		$COOC_5H_{11}$	192	261		0·994		1·494
Benzyl benzoate	Spasmodin Peruscabin Ergol Perudin	$COOCH_2C_6H_5$	212	323	19	1·123		1·568
Butyl benzoate		$COOC_4H_9$	178	250	−22	1·00		1·498
Ethyl benzoate		$COOC_2H_5$	150	213	−35	1·065		1·5068
Ethyl benzyl benzoate				355	58	1·155		
Ethylene glycol dibenzoate		$CH_2OOCC_6H_5$ | $CH_2OOCC_6H_5$	270	360 decomp.	73			

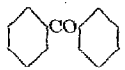
Glyceryl tribenzoate	Mollit B Plastic A Tribenzoin	$CH_2OOCC_6H_5$ | $CHOOCC_6H_5$ | $CH_2OOCC_6H_5$	404		71	1·25		
Glyceryl diaceto benzoate	Mollit A							
Methyl benzoate	Niobe oil	$COOCH_3$	136	199	−12·5	1·103		1·5181
Methyl benzyl benzoate				351	52	1·190		
Phenyl benzoate		$COOC_6H_5$	198	314	71	1·235		
Propyl benzoate		$COOC_3H_7$	164·1	231	−52	1·027		
BORATES								
Amyl borate		$(C_5H_{11})_3BO_4$	288	250–260		0·865		1·42
Butyl borate		$(C_4H_9)_3BO_4$	246	190/220 mm.				
CHLORINATED COMPOUNDS								
Chlorinated diphenyls	Arochlors	See section on this subject						
Trichloroethyl phosphate		$(Cl.C_2H_4O)_3PO$	*285·5*	*210–220* (20 mm.)		1·443	*437*	
Dichloroethyl phosphate	Cetamol QU			210–220		1·427		
CITRATES								
Triamyl citrate		$CH_2COOC_5H_{11}$ | $CH(OH)COOC_5H_{11}$ | $CH_2COOC_5H_{11}$	403			1·013		1·447

CONSTANTS OF PLASTICISERS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (°C.).	M.Pt. (°C.).	S.G.	Flash Pt. (°F.)	R.I.
CITRATES (*cont.*)								
Tributyl citrate		$CH_2COOC_4H_9$ $CH(OH)COOC_4H_9$ $CH_2COOC_4H_9$	361	233/17 mm.		1·050 (18° C.)		1·446
Triethyl citrate	Adinol	$CH_2COOC_2H_5$ $CH(OH)COOC_2H_5$ $CH_2COOC_2H_5$	277	294		1·137 (20° C.)		1·445
Trimethyl citrate		CH_2COOCH_3 $CH(OH)COOCH_3$ CH_2COOCH_3	234	176/16 mm. 285 decomp.	79			
ETHERS								
Dibenzyl ether	Erganol		198	299 approx. decomp.	4	1·035	239	
Diphenyl ether			170	252	28	1·073 (25° C.)		
Glyceryl dicresyl ether	Abracol 242	$CH_2OC_6H_4CH_3$ $CHOH$ $CH_2OC_6H_4CH_3$	272	328–340		1·136		1·549

Glyceryl mono-cresyl ether	Abracol 1011	CH_2OH | $CHOH$ | $CH_2OC_6H_4CH_3$	182	210–230		1·124		1·53
Glyceryl mono-phenyl ether	Autodyne	CH_2OH | $CHOH$ | $CH_2OC_6H_5$	168					
Glyceryl diphenyl ether		$CH_2OC_6H_5$ | $CHOH$ | $CH_2OC_6H_5$	244		80			
GLYCOLLATES								
Butyl phthalyl butyl glycollate	Santicizer B. 16	$C_4H_9OCOC_6H_4COOCH_2COOC_4H_9$	336	219/5 mm.		1·097	390 (open)	1·490
Ethyl phthalyl ethyl glycollate	Santicizer E. 15	$C_2H_5OCOC_6H_4COOCH_2COOC_2H_5$	280	190/5 mm.	20	1·18	384 (open)	1·498
Methyl phthalyl ethyl glycollate	Santicizer M. 17	$CH_3OCOC_6H_4COOCH_2COOC_2H_5$	266	189/5 mm.		1·220		1·504
HYDROCARBONS								
Diphenyl ethane sym.		$(C_6H_5)_2C_2H_4$	182	284	52	0·995		
Diphenyl methane		$(C_6H_5)_2CH_2$	168	260	25	1·06 (25° C.)	130	1·579
Naphthalene		$C_{10}H_8$	128·1	218	80	1·145		
KETONES								
Acetophenone	Mittel HNA	$COCH_3$	120	202	20	1·03	105	1·5341

CONSTANTS OF PLASTICISERS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (° C.).	M.Pt. (° C.).	S.G.	Flash-Pt. (° F.).	R.I.
KETONES (*cont.*)								
Benzophenone			182	305	48	1·108		
Camphor		$C_{10}H_{16}O$	152	204 sublimes	175	0·995	158	
LACTATES								
Methyl cyclohexyl lactate	Sextol lactate			230–255		1·02	208	
LAURATES								
Benzyl laurate		$CH_3(CH_2)_{10}COOCH_2C_6H_5$	290	210/12 mm.	8·5	0·946		
Ethyl laurate		$CH_3(CH_2)_{10}COOC_2H_5$	228	269	−11	0·867 (13° C.)		1·4321
Methyl laurate		$CH_3(CH_2)_{10}COOCH_3$	214	268	5	0·869 (19° C.)		
LAEVULINATES								
Butyl laevulinate		$CH_3COCH_2COOC_4H_9$	158	238		0·9735		1·430
Isoamyl laevulinate				249		0·96		1·431
OLEATES								
Butyl oleate		$C_8H_{17}CH{=}CH(CH_2)_7COOC_4H_9$	338·4	180–195 2 mm.		0·875		
Ethyl oleate		$C_8H_{17}CH{=}CH(CH_2)_7COOC_2H_5$	310·4	206/10 mm.		0·871		
Methyl oleate		$C_8H_{17}CH{=}CH(CH_2)_7COOCH_3$	296·4	216/20 mm.		0·879		

OXALATES								
Amyl oxalate		$COOC_5H_{11}$ | $COOC_5H_{11}$	230	265		0·97		
Benzyl oxalate		$COOCH_2C_6H_5$ | $COOCH_2C_6H_5$	270	235/14 mm.	80			
Butyl oxalate	Losungmittel O Mittel OC	$COOC_4H_9$ | $COOC_4H_9$	202	243		1·001 (0° C.)		1·425
Cyclohexyl oxalate		$COOC_6H_{11}$ | $COOC_6H_{11}$	254	190/10 mm.	40			
Dimethyl cyclohexyl oxalate	Barkite B	$COOC_6H_9(CH_3)_2$ | $COOC_6H_9(CH_3)_2$	310	180–200 (4 mm.)		1·015	293	
Ethyl oxalate		$COOC_2H_5$ | $COOC_2H_5$	146	186	−41	1·103 (0° C.)		1·410
Isoamyl oxalate		$COOCH_2CH_2CH(CH_3)_2$ | $COOCH_2CH_2CH(CH_3)_2$	230	262		0·968 (11° C.)		
Isopropyl oxalate		$COOCH(CH_3)_2$ | $COOCH(CH_3)_2$	174	190		1·010 (18° C.)		

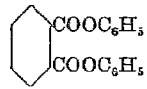
CONSTANTS OF PLASTICISERS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (°C.).	M.Pt. (°C.).	S.G.	Flash-Pt. (°F.).	R.I.
OXALATES (*cont.*)								
Isobutyl oxalate		$COOCH_2CH(CH_3)_2$ / $COOCH_2CH(CH_3)_2$	202	229		1·002 (14° C.)		
Methyl oxalate		$COOCH_3$ / $COOCH_3$	118	163	54	1·422		
Methyl cyclohexyl oxalate	Barkite	$COOC_6H_{10}CH_3$ / $COOC_6H_{10}CH_3$	282	190–200 (10 mm.)		1·035		
Propyl oxalate		$COOC_3H_7$ / $COOC_3H_7$	174	213		1·038 (0° C.)		
PALMITATES								
Benzyl palmitate		$C_{15}H_{31}COOCH_2C_6H_5$	346		36	0·914		
Ethyl palmitate		$C_{15}H_{31}COOC_2H_5$	284·3	185/10 mm.	24	0·858		
Methyl palmitate		$C_{15}H_{31}COOCH_3$	270·3	196/15 mm.	29			
PHTHALATES								
Benzyl butyl phthalate	Palatinol BB	$C_6H_4(COOC_4H_9)(COOCH_2C_6H_5)$	312	208–288 (20 mm.)	383	1·095		
Butyl glycol phthalate				370 (decomp.)				

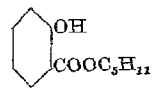
Diamyl phthalate	Placidol A	$COOC_5H_{11}$ $COOC_5H_{11}$	306·1	340		1·026	319	1·4877
Dibenzyl phthalate		$COOCH_2C_6H_5$ $COOCH_2C_6H_5$	346	277/15 mm.	42			
Dibutyl phthalate	Placidol B Elaol Palatinol C	$COOC_4H_9$ $COOC_4H_9$	278·2	340		1·046 (20° C.)	360	1·493
Dicapryl phthalate		$COO(CH_2)_7CH_3$ $COO(CH_2)_7CH_3$	390·3	229/4·5 mm.		0·96		
Dicyclohexyl phthalate		$COOC_6H_{11}$ $COOC_6H_{11}$	330			1·075		
Diethyl phthalate	Placidol C Anazol Solveol Anozol Neantin Palatinol A Suresnol Salvarvol Solvarol	$COOC_2H_5$ $COOC_2H_5$	222·1	176–179 (20 mm.) 298		1·123		1·500
Diethyl hydro-phthalate	Hydrophthalate A Hydropalat A					1·059		
Dibutyl hexahydro-phthalate	Hydrophthalate B Hydropalat B			185–190 (10 mm.)		1·005	304	

CONSTANTS OF PLASTICISERS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (° C.).	M.Pt. (° C.).	S.G.	Flash-Pt. (° F.).	R.I.
PHTHALATES (*cont.*)								
Diethyl glycol phthalate	Softener PA Palatinol E Cellosolve phthalate	$C_6H_4(COOCH_2CH_2OC_2H_5)_2$	310	345	34	1·13	284	
Di-isoamyl phthalate		$C_6H_4(COOCH_2CH_2CH(CH_3)_2)_2$	306·1	349		1·024 (19° C.)		
Di-isobutyl phthalate	Palatinol JC	$C_6H_4(COOCH_2CH(CH_3)_2)_2$	278·2	191–200 (20 mm.) 305–315		1·049	161	
Dilauryl phthalate		$C_6H_4(COO(CH_2)_{11}CH_3)_2$				0·943		1·482
Dimethyl phthalate	Solvarome Grundlage Fermine Palatinol M	$C_6H_4(COOCH_3)_2$	194·1	164–169 (20 mm.) 282		1·196 (19° C.)	132 290	1·5154
Dimethyl glycol phthalate	Mittel PM Palatinol O	$C_6H_4(COOCH_2CH_2OCH_3)_2$	282	209–261 (20 mm.)		1·17	345	

Diphenyl phthalate			318		70			
PHENOLS								
p-tertiary butyl phenol	Abracol 1001		150·1	237	99			
PHOSPHATES								
Triamyl phosphate		$(C_5H_{11})_3PO_4$	308	225/50 mm.		0·950		
Tributyl phosphate	Plastoplex	$(C_4H_9)_3PO_4$	266	270 (decomp.)		0·982	320	1·425
Tricresyl phosphate	Kronitex TCP Plastic X Lindol	$(CH_3C_6H_4)_3PO_4$	368	430–440		1·185	419 428	1·561
Triethyl phosphate		$(C_2H_5)_3PO_4$	182	215		1·064		
Tri-isobutyl phosphate		$(C_4H_9)_3PO_4$	266	264		0·962		
Triphenyl phosphate	TPP Altal Kronilyne	$(C_6H_5)_3PO_4$	326	260/20 mm. 410	50		455	
Tripropyl phosphate		$(C_3H_7)_3PO_4$	224	252		1·002		
Trimethyl phosphate		$(CH_3)_3PO_4$	140	196		1·205		
RICINOLEATES								
Butyl ricinoleate	Baker's P. 3	$CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_7COOC_4H_9$	354	275/13 mm.		0·9058		1·4566
Ethyl ricinoleate	Baker's No. 2	$CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_7COOC_2H_5$	326	258/13 mm.		0·9145		1·4618
Isopropyl ricinoleate		$CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_7COOCH(CH_3)_2$	340	266/10 mm.		0·9083		1·4583

CONSTANTS OF PLASTICISERS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (° C.).	M.Pt. (° C.).	S.G.	Flash-Pt. (° F.).	R.I.
RICINOLEATES (*cont.*)								
Propyl ricinoleate		$CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_7COOC_3H_7$	340	268/13 mm.		0·9079		1·4573
Methyl ricinoleate	Baker's No. 1	$CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_7COOCH_3$	312	245/10 mm.		0·924		1·4588
SALICYLATES								
Amyl salicylate	Plastolin II		208	265		1·065		
SEBACATES								
Dibenzyl sebacate		$(CH_2)_8(COO\ CH_2C_6H_5)_2$	382·3	265/4 mm.		1·06		
Dibutyl sebacate		$(CH_2)_8(COO\ C_4H_9)_2$	314·3	345		0·94		
STEARATES								
Amyl stearate		$CH_3(CH_2)_{16}COOC_5H_{11}$	354	360	30	0·860		1·445
Butyl stearate	Apex No. 4	$CH_3(CH_2)_{16}COOC_4H_9$	340	220–225 (25 mm.) 355–368	19·5	0·865	293	1·444
Cyclohexyl stearate		$CH_3(CH_2)_{16}COOC_6H_{11}$	366	220–240 (4 mm.)	25	0·885		
Ethyl stearate		$CH_3(CH_2)_{16}COOC_2H_5$	312	200/10 mm.	33	0·871		
Methyl stearate		$CH_3(CH_2)_{16}COOCH_3$	298	215/15 mm. 442	38			

Propyl stearate		$CH_3(CH_2)_{16}COOC_3H_7$	326		29			
Methyl cyclohexyl stearate	Sextol stearate	$CH_3(CH_2)_{16}COOC_6H_{10}CH_3$	380	220–240 (4 mm.)	>15	0·887	338	
SUCCINATES								
Dibenzyl succinate	Esterol Benzsuccin *Spasmin*	$CH_2COOCH_2C_6H_5$ | $CH_2COOCH_2C_6H_5$	298	238/14 mm.	42			
Dibutyl succinate		$CH_2COOC_4H_9$ | $CH_2COOC_4H_9$	230	255	−19	0·974		
Diethyl succinate		$CH_2COOC_2H_5$ | $CH_2COOC_2H_5$	174	216	−21	1·049 (15° C.)		1·4200
Di-isoamyl succinate		$CH_2COOCH_2CH_2CH(CH_3)_2$ | $CH_2COOCH_2CH_2CH(CH_3)_2$	258	297		0·961 (13° C.)		
Di-isobutyl succinate		$CH_2COOCH_2CH(CH_3)_2$ | $CH_2COOCH_2CH(CH_3)_2$	230	265		0·974 (17° C.)		
Dimethyl succinate		CH_2COOCH_3 | CH_2COOCH_3	146	195	18	1·120 (18° C.)		1·4197
Dipropyl succinate		$CH_2COOC_3H_7$ | $CH_2COOC_3H_7$	202	246		1·016 (4° C.)		

CONSTANTS OF PLASTICISERS—*Continued*

Chemical Name.	Trade Name.	Formula.	M.Wt.	B.Pt. (°C.)	M.Pt. (°C.).	S.G.	Flash-Pt. (°F.).	R.I.
SULPHONATED COMPOUNDS								
Cresyl *p*-toluene sulphonate	Mittel KP	$CH_3C_6H_4SO_2OC_6H_4CH_3$	262·1	185–195		1·207	365	
Ethyl *p*-toluene sulphonate	Mittel AEP	$CH_3C_6H_4SO_3C_2H_5$	200		32			
TARTRATES								
Diamyl tartrate		$CH(OH)COOC_5H_{11}$ | $CH(OH)COOC_5H_{11}$	290	400 approx.		1·055		1·45
Dibutyl tartrate		$CH(OH)COOC_4H_9$ | $CH(OH)COOC_4H_9$	262	292–312	22	1·092	320	1·442
Diethyl tartrate		$CH(OH)COOC_2H_5$ | $CH(OH)COOC_2H_5$	206	280	17	1·199 (20° C.)		
Dimethyl tartrate		$CH(OH)COOCH_3$ | $CH(OH)COOCH_3$	178	280	48			
UREAS								
Diethyl diphenyl urea	Centralite I Mollit I	$(C_6H_5)(C_2H_5)NCON(C_6H_5)(C_2H_5)$	268	325–330	72	1·11	302	
VARIOUS								
Castor oil						0·958 0·968		1·479
Blown castor oil	Casterol Ricol					0·960 1·00		

CHAPTER 10

DRIERS AND OTHER METALLIC SOAPS

Nomenclature

THE word "drier" is used to describe a wide range of compounds which *include inorganic compounds such as oxides, hydroxides and salts,* soluble metallic salts of organic acids and even solutions of these soluble organic salts. In fact any substance which possesses any dry-stimulating properties is denoted by the term "drier." Moreover, it is not necessary for these substances to be in a condition such that they can assert, immediately, their dry-stimulating properties in order that the above designation may be applied. If, after treatment, they exhibit these properties then they qualify for the designation "drier." Thus, as the term is understood in the varnish trade to-day, a drier is any compound which, in its original form or after subsequent treatment, is capable of assisting catalytically the oxidation and/or polymerisation of any vegetable oil or other composition which dries by oxidation and polymerisation.

The Condition of a Drier

It is important that the drier is in a soluble form for it to exert its catalytic properties. It should be soluble in drying oils both unpolymerised and polymerised, and also in their mixtures with normal varnish resins and thinners.

The true salts of organic acids are the most convenient soluble form of drier, although other soluble complex organic salts are used as driers also. These will be considered at length under lead driers. It does not appear to be absolutely essential for the drier to be soluble, in the true sense of the word, for it is claimed by some that colloidally dispersed metals act as satisfactory driers.[1] This contention is, however, disputed by Krumbhaar, who asserts that colloidal dispersions of metals are without catalytic effect.[2]

Thus the drier must be ideally dispersed as a true solution or possibly it may be effective as a colloidal suspension.

Most metals exert some influence on the drying of oils, and their salts with organic acids are soluble to some degree. Metallic soaps used primarily as driers are frequently used for other purposes. Thus there is no sharp line of demarcation between metallic soaps in general and those used chiefly as driers. For this reason this chapter is devoted to the consideration of both compounds which are popularly accepted as driers, and all other metallic soaps which are used in varnish manufacture for any purpose.

The History of Driers

The history of driers reveals a fascinating development. It shows how the incorporation of driers has developed from the crude and often secret additions of impure, difficultly soluble, compounds, to the use of substantially pure compounds which are readily soluble.

As far as can be ascertained, lead compounds in the form of oxides appear to be the earliest known driers for drying oils. It is recorded that the Egyptians used a mixture of litharge and oil for the mummification of their dead. Galen and Marcellus, in the second and fourth centuries A.D. respectively, mention the use of lead compounds and umber as accelerators for vegetable oils. Jacobus de Tholeto, 1440; Petitot of Geneva, 1644; and Alberti of Magdeburg, 1750, all confirm the use of lead and umber in varnishes. Alberti actually used litharge as a drier for varnishes based on natural copals. The use of lime in drying compositions is described by Eracluis, ninth century A.D., who produced a drying oil from linseed oil by incorporation of litharge and lime. The use of white vitriol (copperas or zinc sulphate) in the preparation of varnishes appeared to be common in medieval times.

The early nineteenth century saw an increase in the number and type of drying compounds. In some surveys of the history of driers, the introduction of manganese as a drier is attributed to Faraday, although Sorel, in 1840, is said to have discovered the drying properties of anhydrous manganese chloride, and to Barruel, 1845, is given the credit for the discovery of the effectiveness of manganese borate. It was about this time also that compounds of lead other than the oxides began to be used. Neil, 1833, is said to have used lead acetate. The next important step in the development of driers was the use of soluble organic salts. Elm [3] places the introduction of fused and precipitated lead and manganese linoleates and resinates as 1885. This was indeed an important milestone in the history of driers. It dealt such a staggering thrust at the use of such insoluble substances as umber, manganese dioxide and red lead, that to-day the use of umber is completely discontinued by every enlightened establishment, whilst manganese dioxide and red lead are almost extinct. It is safe to predict that the passage of another ten years will suffice to relegate these two substances to the position of historical curios only.

It is hard to believe that cobalt, which to-day is, undoubtedly, the most important of our driers, was introduced only at the beginning of the present century. Elm places the discovery of the drying properties of cobalt as about 1901, but a search of relevant literature shows that it was many years after this that it was commonly used. Bottler and Sabin do not include cobalt as a drier in their treatise published in 1912. Vulte and Gibson refer to cobalt linoleate in a paper published in 1902.[4]

Vanadium, cerium, thorium and nickel are newcomers to the field of driers, having been introduced since 1920. Of these, only the two former

have achieved any popularity at all, and these, as yet, are little more than curios. It has not been possible to discover any reference to the use of thorium or nickel in large-scale manufacture.

The next step in the production of the ideal drier was to improve the solubility and stability of the metallic salts of linseed oil fatty acids, tung oil fatty acids and rosin acids. In spite of improvements and modifications these soaps still possess certain unfavourable characteristics, and they have now been partly replaced by metallic naphthenates. When one considers the crude attempts at inducing driers in the past, with the use of naphthenates to-day, the comparison is enlightening.

Mechanism of the Drying Reaction

The precise mechanism of the drying process of drying oils has attracted considerable attention for many years. Whilst it is a subject of absorbing interest which deserves considerable space for adequate treatment, it is beyond the scope of this book. For those who may wish to pursue the subject the following represents a summary of the more important references to workers and theorists: Sacc, Mulder, Jörisen, Reid, Borries, Engler and Frankenstein, Fahrion, Genthe, Wilson and Heaven, Sabin, Fokin, Orloff, Morrell, Kullgren, Rochs, Lidoff and Fokin, Gardner, Friend, Olsen and Rostner, Ingle, Stobbe and Dunhaupt, Wolff, Stransky, De Waele, Salway, Eibner, Klein, Coffey, Langmuir, Marks and Morrell, Blom, Scheifele, Beuerle, Wolff and Zeidler, Ward and France, Taylor and Smull, Ockrent, Morrell and Phillips, Lea, Jány, Blassmann and Barautzkaja, Clewell, Bradley, Gee, Aas, Ellis, Morrell and Davis, Knowles, Lawson and McQuillen, Slansky, Long, Rheineck and Ball, Hughes, Hughes and Rideal, Gamble and Barnett, Overholt and Elm, Blagonravova and Lazarev, Behrer, Gee and Rideal, Wornum, New, Nasini and Ghersa, Rinse, Johnson, and others.[5]

Reactions Involved in the Preparation of Driers

The reactions involved in the preparation of driers may be resolved into the following general types:

I. A reaction between inorganic compounds and esters, the esters being glycerides (vegetable oils). Mixed glycerides may be used.

II. A reaction between inorganic compounds and acids. Acids capable of forming oil soluble salts are very numerous, and the use of many has been protected by patent. Mixed acids are often used.

III. A reaction between inorganic compounds and mixtures of acid and ester.

IV. A double decomposition reaction between water soluble salts, yielding a drying salt insoluble in water, but soluble in organic solvents and drying oils.

V. A reaction between an inorganic compound and the hydroxyl group of an ester, e.g. castor oil.

Varnish Constituents

In addition to driers produced by the above reactions, there are other miscellaneous compounds or agents which influence drying and these will be considered also.

Driers from Inorganic Compounds and Vegetable Oils

I. The reaction occurring between inorganic compounds and vegetable oils on heating is the oldest method of preparing driers. These are commonly described as fused driers.

Inorganic Lead Compounds.—Among the inorganic lead compounds used may be included, canary litharge, a fine bright yellow powder; flake litharge, which is also lead monoxide, but in the form of small orange flakes; powdered litharge, a fine orange powder; red lead, a fine bright red powder; lead acetate, known sometimes as sugar of lead, as white crystals; and lead borate. A lead drier, erroneously described as fused lead linoleate is made by "dissolving" canary litharge, flake litharge or red lead in linseed oil by heating. The reaction with red lead is the most difficult to effect. With it temperatures in excess of 240° C. and vigorous stirring are necessary for the reaction to proceed to an appreciable extent. Even then, under these conditions, substantial amounts of lead remain unreacted. According to some, the litharge content of the red lead reacts readily, leaving lead peroxide. This exhibits very little tendency to react, and is generally wasted. The use of red lead for the production of driers is fast becoming obsolete. Its use is now confined almost exclusively to the production of a few black finishes.

Flake litharge reacts more readily than red lead, but because of its comparatively large particle size it is much less reactive than canary litharge.

The Preparation of Litharge-linseed Oil Driers.—The best technique for preparing lead driers from linseed, tung or similarly constituted oils is to heat the bulk of the oil to a steady temperature of 220°–225° C. The canary litharge which has been carefully dispersed in a little of the oil by passing rapidly through a cone mill, is added slowly as a fine stream with constant stirring. A reaction resulting in the production of a lead compound containing 28–30 per cent lead will be complete in not more than five minutes under these conditions. It should be borne in mind that when grinding or mixing certain grades of litharge with dry linseed oil, heat is developed and spontaneous ignition may occur. This tendency has not been observed with grades of litharge as produced in this country, but comment has been made on the possibility elsewhere.[6] Large agglomerates of litharge do not dissolve readily but usually fall to the bottom of the making pot. Prolonged heating causes darkening.

The Mechanism of the Reaction between Litharge and Linseed Oil.—Explanations of and observations on the mechanism of the reaction between litharge and linseed oil have been put forward by many, including:

Scheele, Sace, Andes, Weger, Ingle, Livache and McIntosh, Diggs and Campbell, Ragg, Charisuis and Kindscher, Kindscher and Lederer, Philadelphia Club, Krumbhaar, and others,[7] but none of these adequately explain the true nature of the reaction involved. The author, with the assistance of M. P. Balfe, has studied the reaction, and the following explanation was evolved, which, in their opinion, accommodates all the experimental facts, besides providing explanations for other phenomena, including the depolymerisation of highly bodied tung oil.[8]

It has been suggested already that the product of the reaction between litharge and linseed oil is not a true lead linoleate, for it is easily possible to obtain lead compounds with lead contents substantially in excess of that theoretically required for normal lead linoleate. Further, although the theoretical amount of litharge only may be used for the reaction, the product is not lead linoleate but a complex mixture, the composition of which will be discussed later. Any ester will react with litharge providing the temperature for the reaction is kept above 195° C. Thus, any vegetable oil is capable of yielding oil or hydrocarbon soluble lead salts. The reaction proceeds in the following stages. The fundamental step in the reaction is the hydrolysis of the ester into acid and alcohol, and the first step in the process is, therefore, to provide water for this to take place. This is derived from the interaction of litharge with any free acid present, and from the oxidation of the ester into water, carbon dioxide and more acid. The oxygen necessary for the oxidation may be derived from the atmosphere, since normally the reaction is conducted with free access to air ; or from the partial reduction of the litharge to lead. Incidentally, lead salts have been shown to catalyse the oxidation. After the water evolved has engaged in the hydrolysis of the glyceride into alcohol and fatty acid, the litharge can react with both products, with the fatty acid to form lead salts and with the glycerol to yield lead glyceroxide. In both cases water is evolved again and is ready to aid in further hydrolysis. When litharge reacts with the fatty acids produced as the result of hydrolysis of linseed oil, lead linoleate is formed momentarily. This, however, can react with more litharge, and basic lead linoleates are formed. Thus when litharge is "dissolved" in linseed oil the product obtained is a complex mixture containing normal and basic lead linoleates and lead glyceroxide. It is, therefore, very different constitutionally from the product obtained by the interaction of litharge with the theoretical amount of linseed oil fatty acids, or the product produced by precipitation from a solution of sodium linoleate. It is interesting to observe, however, that in the production of fused lead linoleate from litharge and linseed oil fatty acids, more than the theoretical amount of litharge can be introduced, and the resulting product is a mixture of normal lead linoleate with basic linoleates.

Both lead acetate and lead borate may be cooked directly into linseed oil, with the object of obtaining driers which are claimed by some to be substantially paler than those obtained by using litharge. It is the

author's experience, however, that provided adequate precautions and care to detail are observed, the products from the litharge reaction are sufficiently pale for all practical purposes, and the use of lead acetate and lead borate for the manufacture of fused driers has almost ceased.

From the above it seems logical that the addition of water to the reaction mixture of litharge and linseed oil should facilitate the reaction, and such additions have been advocated. Any advantages which are gained may be outweighed by the extra care necessary in adding wet litharge to hot oil.

Litharge should be stored in a dry place, preferably out of contact with air. When it gets damp it tends to cake and the lumps formed are difficult to "dissolve". Lead carbonate may be formed which is much more difficult to disperse in oil than litharge.

When litharge and linseed oil are heated to temperatures in excess of 260° C. other secondary complex reactions occur in addition to those already described.

Inorganic Manganese Compounds.—These high temperatures are necessary for the incorporation of manganese dioxide (pyrolusite) in linseed oil. It is hard to conceive how such an inert substance as manganese dioxide was ever used in the manufacture of driers. Considerable heating and stirring are essential to effect any reasonable result, but even so, substantial percentages of the dioxide never react, but congregate at the bottom of the pot and are ultimately thrown away. Manganese dioxide may contain iron as an impurity. Manganese hydroxides which occur as black or brown powders are obtained by precipitation. They are usually fairly pure and dissolve in oil more readily than manganese dioxide. Hydrated manganese oxides may be used also in place of manganese dioxide. Manganese acetate and borate are also used occasionally.

Inorganic Cobalt Compounds.—Cobalt hydrate, a rose pink powder, is a popular cobalt compound for the production of driers by direct interaction with linseed oil. At 260° C., with constant stirring, it reacts readily to give a raspberry coloured syrup. It is easy to follow the extent of the reaction by removing drops on cold glass from time to time. The mixture loses its turbidity, giving place to mere opalescence until finally, when the reaction is complete, it becomes quite clear.

Cobalt acetate may be used similarly, but it is more convenient to use the hydrate which is more economical. In addition, the evolution of large amounts of acetic acid makes the process with the acetate very objectionable, unless a very efficient exhausting system is available. Cobalt borate may be used, but nowadays is rarely encountered.

Cobalt oxide (CoO) is only rarely dissolved directly into linseed oil by heating, although its use in conferring certain properties on oils has been recorded. It is claimed that linseed oil, neutralised with cobalt oxide by heating at 100°–120° C., yields an oil which possesses the property of holding driers in solution better than untreated linseed oil.[9]

The Manufacture of Pale Driers.—Special pale driers are prepared from the hydroxides of metals like calcium, cobalt, lead, manganese and zinc. Great care is exercised in the preparation of the hydroxides which are precipitated at normal or reduced temperatures from aqueous solutions of chlorides, sulphates or acetates. The precipitation is conducted in the absence of air, and the water used for the solutions of the reactants is freed from dissolved air by boiling. The precipitated hydroxides in the form of wet pastes are reacted with glycerides or fatty acids at temperatures not in excess of 200° C. Alternatively, the wet pastes are blended in the absence of air with linseed or wood oil stand oil which acts as a dispersing agent. The mixture is then reacted below 200° C. with glycerides, rosin, naphthenic acid or other suitable fatty acids.

The low temperature precipitation of the hydroxides is claimed to yield compounds in a finely divided colloidal state with enhanced reactivity. Exclusion of oxygen or air during the precipitation, or the subsequent reaction with triglyceride, is stated to aid in the retention of reactivity.[10]

Driers from Inorganic Compounds and Fatty Acids

II. Another common method for the preparation of fused driers is that in which organic acids are reacted with similar inorganic compounds to those used in the production of driers from glycerides. Probably every organic acid capable of yielding oil soluble metallic salts has been examined for its general suitability. Among the commoner acids are the fatty acids from linseed oil and tung oil, rosin, naphthenic acid and oleic acid. Other acids suggested include those from heavy rosin distillates, containing rosin oils of density 0·950–0·995, and pine oils of density 0·935–0·940. These are reacted with metallic oxides to yield salts soluble in turpentine, white spirit or naphtha.[10] Fatty acids from stillingia oil, wool fat (lanolin), coconut oil, or mixed capric, lauric, and myristic acids,[11] sulphonic acids derived from petroleum by treatment with fuming sulphuric acid or sulphur trioxide, acids obtained from vapour phase cracked paraffin (boiling range 30°–300° C.) which is polymerised at 30° C. in the presence of aluminium chloride followed by atmospheric oxidation at 170° C. for 200 hours, acids obtained by oxidation of paraffin or petroleum,[12] and acids obtained from the high temperature and high pressure oxidation under alkaline conditions of the primary alcohols (boiling-point above 140° C.) obtained as by-products in the synthesis of methanol,[13] have also been suggested as the basis for the manufacture of driers. The following represents a short summary of the more complex acids whose use has been recorded in the last few years: acids of the type $ROC_nH_{2n}COOH$, where R may be an alkyl radical with more than five carbon atoms, an aryl radical comprising a side chain of more than four carbon atoms, or a hydroaromatic or terpenic radical, n is one, two or three, e.g. octyl oxyacetic and capryl oxyacetic acid; another reference suggests that n may be four or five;[14] phthalamic acid in which an

amino hydrogen is substituted by the radical of an organic hydroxy compound ; keto aromatic monobasic acids, of which the type

$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(C_nH_{2n-y}){-}COOH$$

is given, wherein R is an aromatic nucleus, n is 2, 3, 4, 5, 6, 7 or 8, and y is zero or two ; aroyl-*o*-benzoic acids of general formula

$$HOOC\,.\,C_6H_4\,.\,CO\,.\,R\,.\,CHX(CH_2)_nCH_3,$$

where R is an aromatic hydrocarbon radical, X a hydrogen or alkyl group, and n is a number greater than unity ; alkylated phenol monocarboxylic acids, completely or partly hydrogenated monobasic derivatives of benzoic acid wherein one hydrogen is replaced by a hydrocarbon radical ; and cyclohexane-1-carbalkyl oxy-1-acetic acid or alkyl hydrogen cyclohexane-1-1-diacetic acid.[15] It is obvious that these complex acids are too expensive to be used generally for the manufacture of driers, and they are, as yet, of academic interest only.

All the foregoing acids have been selected for their property of yielding soluble metallic salts. Other acids are used to yield salts where the chief consideration is not solubility. The salts obtained are not used as driers but find application for special purposes such as flatting and waterproofing agents, etc. These acids include stearic and palmitic acids. Flatting agent, Albertate 175A, is said to be the aluminium soap of a modified phenolic resin.

The Influence of Acid Radical on the Properties of a Soap.—Much has been written on the influence of the acid radical on the properties of metallic soaps. The two chief properties in which the varnish chemist is interested are their influence on drying and solubility. Starting from the basis of a soluble metallic salt, the influence of acid radicals on drying power is still somewhat controversial. The true assessment of their effect is further complicated by the fact that prevailing conditions of temperature and humidity frequently exert profound modifying influences also. The generally superior drying properties of naphthenate driers have been over emphasised only too often by those interested in their distribution, and it is probably true to state that for drying properties, grossly exaggerated claims in favour of naphthenates are not always substantiated in practice. Such claims should be tempered into reasonableness by recalling the fact that cobalt 2-hydroxy-5-isopropyl benzoate catalyses the drying of linseed oil as effectively as cobalt resinate, in spite of the oxidation inhibiting properties of its hydroxyl group, and this tends to bring one to the conclusion that the acid radical may not exert such a profound influence on the drying power as is frequently claimed.[16] Bruson and Stein have produced a comprehensive record of the connection between solvency and structure of the organic acids involved. The

solubility of salts from ketonic acids ($R—CO—(CH_2)_nCOOH$) increases as R increases. Drying salts from aryloxyacetic acids are soluble in petroleum hydrocarbons if the aryl group is represented by benzyl or if the aromatic nucleus has four carbon atoms in the *p* position.

Lead, cobalt and manganese salts from acids of the type

$$R . CO . C_6H_4COOH,$$

where R may be either aromatic or aliphatic, show good solubility in hot oils and aromatic hydrocarbons. The oil solubility of alkylated benzoates is superior to that of corresponding arylated benzoates. The salts of ether acids of the type $RO(CH_2)_nCOOH$ are very soluble, yielding solutions of low viscosity. Polycarboxylic acids yield salts which are generally insoluble in petroleum hydrocarbons. Heat treatment, however, induces solubility in oils but double decomposition occurs.[17] Saturated aliphatic acids yield salts which in the case of low molecular weight acids exhibit solubility in water, whilst with increasing molecular weight water solubility is lost and the salts become practically insoluble in all the usual solvents and oils. Some salts of acids like stearic and palmitic can be dispersed in hot hydrocarbons or vegetable oils, but on cooling either they precipitate from the solution or the solution assumes a gel structure. Salts of high molecular weight unsaturated aliphatic acids such as linoleic, linolenic, elaeostearic, and oleic yield salts soluble in hydrocarbons and oils. Salts of lower molecular weight unsaturated aliphatic acids like crotonic acid are generally insoluble. Saturated aromatic acids like benzoic and hydrocinnamic acids yield very insoluble salts. The introduction of an unsaturated bond does not always confer solubility. Thus, for example, the salts of cinnamic acid remain insoluble.

Since all the drying oils are comprised of mixed triglycerides, involving both saturated and unsaturated aliphatic fatty acids, it is obvious that salts derived from their component fatty acids will consist of a mixture of soluble and insoluble salts.

Fused Linoleates, Tungates and Oleates.—These are prepared by the direct interaction of metallic compounds and the corresponding fatty acids. The reaction proceeds more readily than with linseed oil itself and lower temperatures can be used.

In most of these preparations appreciable bubbling and frothing occurs due to the evolution of water, acetic acid, etc., and care must be exercised to avoid the reaction getting beyond control temporarily. Where the reaction is vigorous the metallic body should be added slowly, and subsequent additions made only when the reaction has subsided from the previous addition. Usually the froth can be beaten down by stirring vigorously from the top.

Canary litharge is most satisfactory for the production of lead linoleate and dissolves readily at 150° C. In general, the inorganic metallic compounds used for interaction with the oils themselves, as described already, can be used with acids, and these include litharge, lead acetate,

lead borate and lead hydroxide. Manganese linoleates are made from manganese dioxide, hydroxide, borate and acetate. Manganese dioxide needs temperatures of 220°–250° C. to effect a satisfactory rate of reaction. Cobalt linoleates are made from cobalt hydrate or cobalt acetate. Calcium and zinc linoleates are made from calcium oxide and calcium hydroxide or zinc oxide respectively. Tungates, oleates, stearates and palmitates are made by similar means from tung oil fatty acids, oleic, stearic and palmitic acids.

Fused Resinates.—These are made by the interaction of rosin with the types of inorganic metallic compounds already mentioned. Thus litharge reacts readily with rosin at 200° C. to yield lead resinate. The temperature of the reaction mixture may have to be raised above 200° C. to obtain a clear product. Manganese dioxide is still used for the production of manganese resinate and temperatures of 240°–250° C. are the most satisfactory. Cobalt resinate is made from cobalt hydrate which reacts satisfactorily at 200° C., although again higher temperatures may be used to effect clarity.

Probably the most important fused resinate is calcium resinate, commonly known as limed rosin. The bulk of the limed rosin produced is in the form of a white spirit solution. In this condition it is described as gloss oil. Considerable quantities of gloss oil are used in many types of cheap paints. Much attention must be devoted to the selection of the raw materials for the production of limed rosin if a good quality product is required. A good pale clear grade of rosin should be selected. It should be free of powder which has a tendency to become oxidised. In this oxidised condition it has inferior solubility and yields dark soaps.

Wood rosin may be used for production of limed rosin, and American grades contain 89–92 per cent abietic acid. In preparing limed rosin from wood rosin the use of a catalyst like lead or calcium acetate is an advantage, and slightly more than normal quantities of lime are used. If a mixed zinc-calcium resinate is desired it is recommended that the zinc oxide is added before the lime. With ordinary gum rosin this precaution is unnecessary.[18]

Either calcium oxide (quicklime) or calcium hydroxide (slaked lime) may be used as the source of calcium. Both materials may contain impurities. High calcium limes should be selected, since these contain less than 5 per cent of magnesia. Other impurities which may be present in the lime include alumina, iron oxide and silica, all of which are undesirable for the production of limed rosin.

If limestone used as the starting material for the manufacture of lime is underburnt, carbonates of calcium and magnesium may be present. On the other hand, if the limestone is overburnt the lime may react with the impurities to form silicates and aluminates which are not soluble. A good lime should yield a clear resinate, although the usual product obtained is slightly opalescent, due to the presence of insoluble impurities.

The usual method adopted for the manufacture of limed rosin is to melt the rosin to a temperature of approximately 200° C. The lime is then added slowly because the reaction is accompanied by considerable bubbling and frothing. The mixture should be stirred continuously, preferably with a stirrer comprising two blades, one at the bottom of the vessel to prevent lime caking there, and the other arranged so that it just cuts the surface of the mixture with the object of checking the rise of the froth. If the lime falls to the bottom of the vessel it tends to cake and it then becomes very difficult to complete the reaction. When all the lime has been incorporated and the frothing has subsided, the temperature may be raised cautiously to 230°–240° C., if desired, to ensure that the reaction is complete. If, however, much unreacted lime remains in suspension it may suddenly react at the higher temperature, after apparent unreactivity, with exceptional violence. It may get beyond control. It is, therefore, emphasised that the final heating is carried out with very great care. The molten limed rosin may be run out to cool or it may be cooled to 180° C. and thinned with white spirit. If the resultant solution is slightly opalescent it may not be possible to eliminate this even by filtration.

Zinc resinate has promise of becoming a useful raw material, not so much for use as a drier but as a hard type resin. A number of grades of zinc resinate are specially manufactured with varying zinc contents and their properties are discussed later.

Zinc oxide reacts readily with molten rosin to yield zinc resinate. Rakutz has reported that the reaction also proceeds to completion in the presence of linseed oil to yield a neutral resinate.[19]

Fused Naphthenates.—Naphthenic acid is the most valuable organic acid at present used in the manufacture of drying and other soaps. It is obtained chiefly from crude petroleum originating in Rumania, Russia and America, although Klebsattel[20] states that it is present in all petroleums. It varies in amount from mere traces to as much as 2·4 per cent of the crude oil. Commercial naphthenic acid is chiefly a mixture of monobasic acids containing the pentamethylene nucleus with the empirical formula $C_nH_{2n-2}O_2$.

Acids of high molecular weight have, however, been obtained from crude naphthenic acids with the empirical formula $C_nH_{2n-4}O_2$, and these are believed to be binuclear acids with two cyclopentane rings joined together.[21]

Work has been conducted on the establishment of the chemical structure of naphthenic acids by Aschan, Markownikow, Zelinsky, Engler and Tanaka.

Among the fractions obtained from the distillation of crude petroleum are those containing kerosene and gas oil. The naphthenic acids are in these fractions, and are obtained by neutralising with dilute sodium carbonate solution, separating the aqueous solution and setting free the acids by addition of sulphuric acid. Another method of obtaining the

acids consists in washing crude petroleum oil with sulphuric acid and then extracting with caustic soda solution which dissolves out the naphthenic acids. These are recovered, as in the first process, by re-acidifying,[22] or naphthenic acids obtained by distillation of crude oil are neutralised with caustic soda. The mixture is allowed to stand and tarry matter is removed. The residual solution is then extracted with solvent to remove more sludge and is subsequently treated several times with sulphuric acid.[20]

A fourth process which is used to extract naphthenic acids from the petroleum fractions containing them is to distil these fractions in the presence of sodium alkali. This results in the production of sodium naphthenate which with some mineral oil is left behind in the still. The sodium naphthenate being soluble in 80 per cent alcohol is extracted with this solvent, the alcohol removed by distillation and the naphthenic acids regenerated by acidifying.[21]

Sodium naphthenate is a powerful emulsifying agent, and this leads to the inclusion of certain impurities in the resulting naphthenic acid. Normally these crude naphthenic acids are subjected to distillation if they are to be used for the manufacture of driers. They may be redistilled and fractionated. It is known that certain manufacturers of naphthenate driers select their acids with great care in order to obtain drying salts with certain properties, and it is probable that these acids with specified properties could be obtained only by fractionation of the crude acid mixture. Thus cobalt naphthenate is stated to be best if produced from acids of boiling-point about 270° C.,[23] whilst for lead and manganese a boiling range of 280°–300° C. is recommended.

Davydov and Mizne give details of a material which they describe as pure acidol, which is derived from crude naphthenic acid by distillation. It is the fraction boiling range 115°–140° C. at 35/50 mm. which is selected, and this possesses the following constants, sp. gr. 0·925, acid value 230, saponifiable 73·4, iodine value 6·2, ash 0·0 per cent.[24]

Two grades of naphthenic acid are generally available in this country as liquids, varying from a straw to a brown colour. Details of these grades are given in the table below. If the naphthenic acid of commerce

PROPERTIES OF COMMERCIAL NAPHTHENIC ACIDS

	N.A. 17	N.A. 9
Min. acid value	170	230
Unsaponifiable matter	Max. 15 %	Max. 10 %
Ash content	0·2 %	0·2 %
Colour	Dark	Dark

(By courtesy of Technical Products Ltd.)

is fractionally distilled at 13 mm. pressure, a fraction boiling at 150°–180° C. can be obtained with an acid value of 275. This permits the manufacture of a lead naphthenate containing 34 per cent of lead.[25] An

even finer fractionation would yield acids with acid values in excess of 275. Thus octonaphthenic acid ($C_7H_{13}COOH$) has an acid value of 400 which yields lead naphthenate of lead content 42·5 per cent.

Low acid value acids are especially recommended for the production of the naphthenates of sodium, potassium, zinc and aluminium. The sodium and potassium salts possess excellent emulsifying properties.

In the laboratory examination of naphthenic acids, Klotz and Littmann point out the disadvantages of assessing the value of the acids on the determination of unsaponifiable portions alone. The normal method of unsaponifiable determination by extraction of an alkaline solution of sodium naphthenate with petroleum ether or other solvents tends to give inaccurate results. The inaccuracy is due to the presence of low boiling unsaponifiable material which may be lost by volatilisation during evaporation of the extracting solvent, and further, non-carboxylic acid phenols may be retained in the alkaline solution.

A method of analysis described, involves extracting the unsaponifiable matter from a sodium naphthenate solution and recovering the acids which are titrated. The acid value of the original acids and that of the purified acids may be determined, and the total acid content estimated. Detailed analysis of commercial naphthenic acids are recorded by the above authors.[26] Naphthali has given some methods of identification of naphthenic acids.[27]

Fused lead, cobalt and manganese naphthenates may be produced by the direct interaction between naphthenic acid and litharge or lead acetate for the lead salt, cobalt hydrate or cobalt acetate for the cobalt salt, and manganese dioxide, manganese hydroxide, manganese acetate or manganese borate for the manganese salt. A mixed drying soap is made from acidol by heating twenty-five parts of acidol with five parts litharge and seven parts of manganese borate respectively at 110°–130° C. for fifteen minutes. A pale drier soluble in white spirit is obtained.[24] Zirconium naphthenate is made by heating zirconium sulphate with naphthenic acid.[28]

Other Fused Metallic Soaps.—Driers are also made from the fatty acids of wool grease. The acetates of cobalt, lead, manganese or zinc are heated with wool grease fatty acids at 150°–160° C. with constant stirring until all reaction has ceased as evidenced by disappearance of the smell of acetic acid.[29]

A drier containing mixed acids is made by heating 250 parts naphthenic acid and 750 parts of wool grease acids at 150° C., at which temperature 260 parts of litharge are added.

Soluble metallic salts are made also from coconut oil fatty acids, and these include the salts of lead, manganese, copper and cobalt. In cold naphtha these salts remain as a fine suspension, but at 100° C. clear solutions are obtained which show no precipitation after cooling for several hours.[11]

All the foregoing descriptions of the preparation of fused driers

concern the direct interaction between the inorganic metallic compounds and the organic acids. Modifications of the conditions of the same fundamental reaction appear in the following examples. Thus titanium stearate is derived from the reaction between titanium tetrachloride and organic acid in the presence of calcium carbonate.[30]

Organic salts of other metals in Group 4A of the Periodic Table may be produced by this method, and the presence of calcium carbonate does not seem to be always essential. Stearates may be produced at 70°–110° C. Hydrochloric acid is evolved.[31]

Driers Prepared in the Presence of Solvent.—Another popular modification is to conduct the reaction in the presence of a solvent for the reaction product. A solution of organic acid in a volatile organic solvent is reacted with a metallic oxide or hydroxide. Water eliminated during the reaction is removed by distillation.[32] A mixture of naphthenic acid with an ether acid of the formula $R—O—C_nH_{2n}COOH$ is reacted with drying metal compounds such as oxides, hydroxides, acetates or carbonates in the presence of an organic solvent. Organic solvents for the reaction products include aliphatic or aromatic hydrocarbons. The ether acid may be octyloxyacetic acid.[14] A rosin solution in naphtha containing a little linseed oil is reacted with cobalt hydrate and calcium hydrate to yield a terebine. Other metallic driers may be made by the same process.[33] In other methods of drier manufacture both water and organic solvents are used. Thus a metallic salt may be dissolved in water and reacted with a solution of organic acid (naphthenic, abietic or linseed oil fatty acids) in mineral spirits, xylol or pine oil.[34] A water soluble resinate is made by adding an aqueous solution of caustic soda to a solution of rosin in petrol. When neutralisation has been effected an emulsion is formed, which is added to hot paraffin (190°–200° C.). Petrol and water are distilled off and granular sodium resinate is precipitated.[35] Lead capryloxyacetate, which is soluble in aromatic hydrocarbons, is made by adding capryloxyacetic acid to lead nitrate solution. Other ether acids of the type $R . O . CH_2COOH$ may be used.[14]

Driers from Inorganic Compounds and Mixtures of Acids and Esters

III. Fused driers may be made by the interaction of inorganic metallic compounds with mixtures of acids and esters. Thus hydroxides of metals including those of calcium, cobalt, zinc, manganese and lead specially precipitated under non-oxidising conditions, as explained already, are used. Cobalt hydroxide is precipitated from a solution of cobalt sulphate, removed by pressing and washed with air-free water. The wet precipitate is then converted into a paste with linseed stand oil by kneading and the resultant product subjected to vacuum. The ester in this example is the linseed oil stand oil. The oil paste is reacted at 95° C. with a 50 per cent rosin solution in mineral spirits.[10]

Using a similar dispersion of precipitated hydroxide in oil, the same is

reacted without drying, below 205° C., with naphthenic acid, rosin or other fatty acids.[36]

Work has been conducted on the reaction between rosin and zinc oxide in the presence of linseed oil. Rakutz states that below 300° C., no reaction occurs between zinc oxide and linseed oil. He gives the melting-points of zinc resinates prepared in the presence of increasing amounts of linseed oil. The melting-points of the products decreased with increasing amounts of oil. Rosin, 100 parts and zinc oxide, 12 parts, gave melting-points of 103° C., 96°, 86°, 82°, 77°, 72°, 67°, and 65°, when the linseed oil present was 15, 20, 25, 30, 35, 40, 45 and 50 parts respectively.[19]

Precipitated Driers

IV. These are made by the interaction of a water soluble salt of an organic acid with a water soluble salt of a drying metal. The sodium, potassium and ammonium salts of the organic acids may be used, whilst the salts of the drying metals are usually chosen from acetate, sulphate, nitrate and chloride. Organic salts of the following metals may be obtained by double decomposition, lead, cobalt, manganese, cerium, titanium, thorium, zirconium, aluminium, lanthanum, vanadium, zinc, nickel, copper, iron, tin, calcium, magnesium, barium, strontium, cadmium, mercury, silver, bismuth, and chromium. Organic acids yielding salts of alkali metals soluble in water include fatty acids from linseed, tung, perilla, soya bean and stillingia oils, wool fat (lanolin), and rosin, naphthenic acid, stearic acid, oleic acid, palmitic acid, cyclohexane-1-carbalkyloxy-1-acetic acid, and alkyl hydrogen cycloxhexane-1-1-diacetic acid.

The method used for the preparation of precipitated driers, except for minor modifications, may be described as follows. The sodium salt of the organic acid is first prepared. Thus for linoleates, tungates, etc., the calculated quantities of the corresponding acids and caustic soda are heated together with water. The procedure is the same for resinates from rosin, or for any other acid. To avoid using fatty acids from drying oils it is cheaper to saponify the oils with the caustic soda solution. This necessitates a boiling of an hour or more with constant stirring to effect saponification. Fresh additions of water may have to be added from time to time to compensate for losses during boiling and to prevent the mass of soap from becoming unmanageably thick. With direct fired vessels the tendency of the soap solution to burn on the bottom of the boiling vessels increases as the saponification approaches completion, and this explains why it is so important to keep the mass constantly moving. Jacketed vessels using superheated steam do not suffer from this disadvantage. After the formation of the sodium salt, unsaponifiable matter often remains undissolved, and may be removed at this stage. Thus with an aqueous sodium naphthenate solution a dark tarry scum may float at the surface and this may be removed by straining through fine muslin, often without cooling the bulk of the liquid. Whilst the

solution of the sodium salt is being made, a hot aqueous solution of the metallic salt is being prepared simultaneously. It is common practice to prepare enough metallic salt solution based on calculation, to effect complete precipitation with the sodium salt, plus a slight excess. The hot metallic salt solution is then added to the boiling sodium soap solution until the mother liquor just becomes neutral to litmus. The water is decanted or separated from the precipitated soap which is then washed free of water soluble matter by boiling with successive lots of clean water.

Dehydration by Heating.—After the final washing as much water is removed as possible, and the residual, partly dried, precipitated soap is slowly heated with stirring to remove all occluded water. Continual stirring is necessary to avoid overheating of the viscous soap and to prevent charring, which results in loss of colour. The heating is continued until the temperature reaches 115°–120° C., when it may be assumed that the soap is substantially dry, all the water having been expelled.[37]

Some processes use temperatures of 130°–140° C., although normally these would appear to be unnecessarily high. Others obtain more rapid and more complete dehydration by heating the metallic soaps under vacuum. Suction filtration, followed by drying at low temperatures (40° C.), has been used, although not extensively. Greenfield states that at 130°–140° C. and atmospheric pressure, fifteen hours are necessary for dehydration, but under light vacuum the duration of heating is reduced to seven hours.[38] Heating is continued for much shorter periods than this in practice, it being considered to have given satisfactory dehydration after treatment of the order of one hour's duration.

It is very important that the heating to effect dehydration is curtailed as much as possible, since these metallic soaps have a pronounced tendency to darken in colour, and with salts of drying oil acids oxidation occurs, producing skinning with its attendant insolubility.

The soap, whilst molten, is poured into containers or thinned with petroleum hydrocarbons to yield terebines.

Stillingia oil is saponified with caustic soda and metallic stillingates are obtained by addition of nitrates. Stillingates of nickel, copper, zinc, cobalt, iron (ous), tin (ous), barium, strontium, calcium, lead, cadmium, mercury (ous) and silver are obtained by this method.[39] The linoleates, tungates, resinates or stearates of thorium, titanium or zirconium are made by interaction of their salts with aqueous solutions of the sodium, potassium, or ammonium salts corresponding with the acids in the above soaps.[40]

In making a mixed soap from wool fat and naphthenic acid, the wool fat is first saponified with an excess of caustic soda. When the saponification is complete the excess alkali is neutralised by the addition of naphthenic acid. Metallic salts of drying metals are then added to precipitate the required soaps.[41]

The Use of Neutral Fluxes.—The drying process is not easy, and varies considerably for different soaps. Some soaps, like lead, cobalt and zinc

naphthenates fuse easily above 100° C. and remain in a convenient fluid state throughout the dehydration. Manganese and aluminium naphthenates, to quote but two examples, do not melt easily and tend to gel. This results in decomposition. Attempts to facilitate the dehydration have been made by modifying the conditions of precipitation or by adding fluxes and other substances to the soap, just before dehydration to keep it liquid.

Thus plasticisers are added to aluminium, zirconium, cerium, lanthanum and vanadium naphthenates to maintain the soaps in molten condition during dehydration.[42]

Plasticisers which have been used include tricresyl phosphate, triethyl citrate, tributyl citrate,[43] *p*-toluene sulphonamides, dialkyl phthalates, benzyl acetate, benzyl benzoate, butyl stearate and drying, semi-drying or non-drying oils.

Acid Fluxes and Stabilisers.—Many so-called oil soluble metallic soaps do not give stable solutions either in oils or hydrocarbons. Stability is noticeably better in aromatic hydrocarbons than in aliphatic hydrocarbons. Instability of solution manifests itself either by yielding solutions which are highly viscous where the soap is in semi-colloidal dispersion only, or by yielding a solution which is initially apparently satisfactory but which, on standing, gels, or precipitates part of the soap. Many fluxes, especially those of acid type, perform the dual rôle of inducing fluidity during dehydration as well as improving stability of solution in oil or hydrocarbons.

Where the additions are to act as stabilisers of solution only they may be added to the dehydrated soap, whilst in the molten state at the time of the preparation of the solution, or after solution has been effected. Where they are expected to perform the dual rôle they are added during the course of the initial precipitation of the soap,[44] or just prior to dehydrating the precipitated soap.

The following acids have been suggested: fatty acids from drying oils such as those from linseed oil, stearic,[44] palmitic,[12] benzoic, cinnamic, crotonic, anthranilic and hippuric [12] acids, mixtures of amino phenyl acetic and benzoyl benzoic acids, mixtures of anthranilic and hydrocinnamic acids, and salicylic acid.[45] Other mixtures of acids protected by patent are mixtures of stearic, mandelic and cinnamic acids, mixtures of palmitic and benzoic acids, mixtures of crotonic and arachidic acids, and mixtures of hippuric and salicylic acids. Benzoic acid and linseed oil fatty acids are probably the most popular stabilisers or fluxes because of their availability, effectiveness and comparative cheapness. The amounts of stabilisers or fluxes which are generally used are fractional percentages for low molecular weight organic acids like benzoic, and as much as 5–10 per cent for the higher fatty acids calculated on the metallic soap. For cobalt linoleate or naphthenate, ½ per cent of benzoic acid or 5 per cent of linseed oil fatty acids are effective. One protected process describes the use of up to 10 per cent of these acids. For cobalt naphthenate,

stearic acid is suggested ; for cobalt-lead linoleate a mixture of anthranilic and hydrocinnamic acids is used ; and for lead-manganese soap from mixed naphthenic and soya bean fatty acids a mixture of aminophenyl acetic and benzoyl benzoic acids is used.[44] Another process definitely suggests the use of about 10 per cent of certain organic acids among which is included benzoic acid. Practical experience has shown, however, that the addition of such large quantities is unnecessary.[12] Six to 10 per cent of saturated fatty acids, such as palmitic acid, are recommended for cobalt linoleate, resinate or naphthenate.[45]

Boner has recorded the results of experiments on the solution or dispersion of metallic soaps in fatty acids. Many of the soaps used were salts of saturated acids. Thus aluminium stearate (0·4 per cent) and calcium stearate (1·71 per cent) were dispersed in cottonseed fatty acids at 150° F. and showed no separation. Neither aluminium oleate (0·92 per cent.) nor lead naphthenate (3·8 per cent) showed any separation after dispersion under similar conditions. Calcium stearate (0·95 per cent) and magnesium stearate (2·22 per cent) were dispersed in tallow fatty acids without separation. Aluminium stearate (1·53 per cent), calcium stearate (0·99 per cent) and aluminium oleate (1·42 per cent) were dispersed in oleic acid at 150° F. and showed no separation. Magnesium stearate (3·81 per cent) and lead naphthenate (11·8 per cent) were dispersed in abietic acid at 375° F. and showed no separation.

Similar work by Baldwin with metallic soaps in oleic acid led him to the conclusion, from freezing-point determinations, that true solutions of the metallic soaps were not obtained, merely dispersions.[46]

Basic Stabilisers.—Sometimes basic stabilisers are used, such as ethanolamines,[12] and trimethylene diamine.[47] The use of 10 per cent of triethanolamine has been suggested. When driers are made from organic acids containing seven carbon atoms and salts of drying metals, the reaction may take place in the presence of an amine in amount from ½ to 1½ molecular proportions based on the acids.[48] The three examples given below are typical of the use of amines in drier manufacture. Cobalt naphthenate is precipitated from a solution of sodium naphthenate by means of cobalt sulphate solution. After removal of all water soluble material by washing, the metallic soap is dehydrated by fusion and triethanolamine is added. Or the mixed linoleates of lead and cobalt are obtained by adding lead nitrate and cobalt sulphate solutions to a solution of sodium linoleate. After washing, trimethylene diamine is added to the precipitated soap and the whole dehydrated under vacuum. In the preparation of aluminium naphthenate, aniline and aluminium sulphate solution are added to a solution of potassium naphthenate. The precipitated naphthenate is washed, ethanolamine is added and the whole subjected to dehydration.[47]

The centrifuging and drying of precipitated zinc tungate and other soaps is assisted by adding 1 per cent of glucose or sugar to a thin wet paste of the precipitate.[49]

Dehydration by Solvent Treatment.—Sometimes dehydration is effected by distillation. The bulk of the water is decanted from the precipitated soap to which a solvent like white spirit or benzene is added. The whole is then subjected to distillation, during which the water in the soap is carried away with the solvent distillate, ultimately leaving the dried soap in solution.

Other methods of drying precipitated soaps are used to avoid long fusion. For example, precipitated soaps which are flocculent and not sticky are merely washed with alcohol to displace the water present and used in the form of paste. Faucett points out the economy in time and labour effected.[50] There is an additional advantage in using precipitated soaps in the paste form, and it is that the tendency for these light fluffy powders to blow about during transit or transference is completely eliminated.

An ingenious method of avoiding dehydration by fusion is to precipitate the drying soaps in the presence of a liquid which is immiscible with water and a non-solvent for the initial reactants, but which is a good solvent for the reaction product. Thus an aqueous solution of a drying salt, together with a hydrocarbon solvent, are agitated together and an aqueous solution of the soap is allowed to flow into the mixture.[51] The drying soap is dissolved in the solvent immediately it is formed, and the other water soluble salts derived from the reaction go into the water solution. This process obviates both washing and drying of the precipitated metallic organic soaps, and the process is conducted at ordinary temperatures. Discoloration due to heating is also avoided. The solvent layer is separated from the aqueous layer, and if solvent-free drying soap is required the solvent is removed by distillation. The following examples extracted from the original patents illustrate the manufacture of various driers based on this method. A solution of lead acetate in water is agitated thoroughly with mineral spirits, and an aqueous solution of sodium naphthenate is added. Using a similar process with aqueous solutions of cobalt chloride ($CoCl_2$, $6H_2O$), silver nitrate, ferric sulphate ($Fe_2(SO_4)_3 9H_2O$), manganese chloride ($MnCl_2 . 4H_2O$), nickel chloride ($NiCl_2 . 6H_2O$), zinc sulphate ($ZnSO_4 . 7H_2O$), copper sulphate ($CuSO_4 . 5H_2O$), aluminium sulphate ($Al_2(SO_4)_3 . 18H_2O$), mercuric nitrate, chromic nitrate, barium hydroxide, and stannic chloride the corresponding drying soaps are obtained. Calcium naphthenate is made by adding a solution of potassium napththenate to a mixture of xylol with a milky dispersion of calcium sulphate in water. In addition to mineral spirits and xylol, pine oil or a mixture of mineral spirits and xylol can be used as solvents. Driers containing two metallic radicals can be made by preparing an aqueous solution containing both metallic salts. These are then reacted simultaneously with the alkali naphthenate, or a mixture of zinc linoleate and naphthenate can be obtained by adding mixed sodium linoleate and potassium naphthenate solutions to a mixture of aqueous zinc sulphate and xylol. Similarly,

mixed naphthenate and resinate can be obtained by using a mixture of aqueous potassium naphthenate and resinate.

Solutions of Driers.—It is obviously most economical to dissolve driers in solvents whilst they are still molten after the dehydrating process, or as soon as they are precipitated, e.g. when solvent is present at the commencement of the precipitation. If a cold concentrated drier is dissolved by subsequent warming then both heat and labour are expended unnecessarily, in addition to possible loss of colour.

Impurities.—Commercial metallic soaps obtained by precipitation may contain small amounts of several different impurities. These may include free fatty acid, unsaponified oil, drying metal salt, sodium or potassium salts of the fatty acid, other inorganic sodium or potassium salts, metallic hydroxides and moisture.

Driers from Castor Oil

V. Another interesting type of drying compound is derived from castor oil or any other oil containing a hydroxyl group. Castor oil is reacted with a metal or metallic compound at high temperatures (up to 250° C.) so that the hydrogen atom of the hydroxyl group of the oil is replaced by metal. Drying compounds such as the cobalt (8 per cent Co), manganese (5 per cent Mn), and lead (29 per cent Pb) compounds have been obtained by this method. They are stated to be soluble in turpentine or in linseed oil at 100° C.[52]

Introduction of Driers and Metallic Soaps

Driers are introduced to varnishes by several different methods. They may be added directly to the hot varnish in the form of inorganic compound or soluble organic salt. Where extreme paleness of product is required the driers are usually added in the cold after the varnish has been thinned. An old method was to attempt to effect solution of the driers by what is known as a " cold drumming " process. In this, driers like litharge and zinc sulphate are added to the varnish and the whole agitated for several days in a rotating drum. The method is very unsatisfactory. Whilst it is true that pale varnishes are obtained, substantial percentages of the initial driers remain undissolved even after prolonged drumming, and are finally relegated to the rubbish heap. The method has now become almost extinct. The best method of adding driers to maintain paleness of colour is in the form of terebine, which is merely a solution of soluble metallic soap in white spirit or other convenient solvent. The terebines must obviously be made as pale as possible, and solution in white spirit, etc., is best effected by dissolving the soap whilst it is still hot and molten after the dehydration process. Alternatively, the soap may be precipitated in the presence of white spirit. This yields very pale terebines because the application of heat is eliminated altogether.

Solutions of soaps like aluminium stearate need much manipulative

ability to obtain really homogeneous solutions in white spirit, naphtha, turpentine, etc. One satisfactory procedure is to mix the stearate with a little of the solvent to give a smooth paste, the solvent always being added to the soap. Small additions are made at a time and each addition thoroughly incorporated before the next is made. When it is certain that all lumpy agglomerates have been dispersed, more solvent is carefully stirred in to yield a very thin paste. Then with constant stirring the mixture is slowly heated. Constant stirring is essential, for if the mixture is allowed to remain undisturbed on the bottom of the vessel gelation may occur and the gelled lumps cannot be redispersed. The heating may be conducted, with advantage, in a jacketed vessel heated by steam or superheated steam. As the temperature is slowly increased it reaches a point in the range 50°–100° C. approximately, depending upon the soap in question, at which the cloudiness or opalescence of the mixture gives place to clarity. At this point a considerable increase of viscosity usually occurs. The remainder of the solvent may then be stirred in to give a solution of convenient viscosity. An alternative method is to sift the dry finely powdered soap gradually into the solvent which is agitated. When all the soap is added the whole is gradually heated with continuous stirring. With soaps like aluminium stearate not more than about 5 per cent can be obtained in solution without the production of inconveniently high viscosities. With some metallic soaps, for example, the naphthenates of manganese, zinc and cerium, the introduction of a few per cent of butyl alcohol to the chief solvent, frequently results in a very substantial lowering of viscosity, in addition to conferring stability on the solutions. Aromatic hydrocarbons are generally better solvents than aliphatic hydrocarbons, as evidenced by the lower viscosities of the solutions obtained with them.

Other Compounds and Factors which Influence Dry

Lead phenoxides are claimed to be capable of use as driers. Organic lead compounds (PbR_4) in a solvent are reacted at 75°–175° C. in the presence of a silica gel catalyst with phenols to yield phenoxides. Thus from lead tetra-ethyl and phenol, triethyl lead phenolate is obtained, and if phenol is replaced by resorcinol, bis triethyl lead resorcinolate is obtained.[53]

Basic lead soaps are also used as driers. Basic lead naphthenate is prepared, and this is reacted with a non-basic soap such as normal cobalt and manganese naphthenate or lead resinate, to yield a drying composition which is still basic but whose basicity is less than that of the original basic lead compound. Or commencing with a basic lead drying salt, it is reacted with a compound providing a reactive carboxyl group so that a product is obtained of reduced basicity but yet is still basic.[54]

Tamamushi and Tohmatou have reported on the catalytic properties of phthalocyanines.[55] Menthol, α-ionone, safrole and iso-eugenol [56] are said to be pro-oxidants for vegetable oils. Menthol was found to reduce

the induction period of linseed oil almost by half. Fawcett states that pro-oxidants can be obtained from soya bean or cottonseed oils by molecular distillation.[57] Salicylic and *p*-amidobenzoic acids are also stated to have some drying action.

Polymers obtained by subjecting a mixture of ethylene and acetylene to a high temperature (230° C.) at high pressure (500 atmospheres) are claimed to promote the drying of vegetable oils.[125]

The value of peroxides as accelerating agents is well known. Substances such as benzoyl peroxide or per salts which liberate oxygen at relatively low temperatures have been suggested.[58] Krumbhaar has explained the influence of the peroxides present in old turpentine on the dry of drying oils,[59] a phenomenon which is observed only in the presence of the normal metallic driers. The higher the peroxide content, the shorter the drying time. Tetralin, dipentene and pine oil behave similarly to turpentine. Fresh turpentine contains about 0·5 mg., and old turpentine about 1·0 mg. of peroxidic oxygen per c.c. If turpentine is blown the peroxidic oxygen content can be increased to 2·5 mg. per c.c. According to Krumbhaar the theory for the phenomenon is that the valency of the metallic drier changes, due to oxidation and reduction, resulting in evolution of oxygen which is absorbed by the drying oil.

It is well known that temperature has a very important influence on the rate of dry of oil films, and it need not be elaborated here. The presence of ozone is also distinctly advantageous. Small traces of ozone in admixture with air under conditions of elevated temperature produce, according to Kufferath, a reduction in drying time of two-thirds. Karsken confirms that at ordinary temperatures ozone appreciably reduces the drying time of linseed oil paints.[60] The presence of volatile bases in the air is stated to reduce drying time by one half. Ammonia (0·2–0·3 gm. per c.m.) has this effect.[61]

Another factor influencing speed of dry is light. It is common knowledge that oxidisable films dry slower in the absence of light. Genthe has given confirmatory evidence on the accelerating influence of ultra-violet light.[62]

Drying oils set more quickly in the presence of ionised oxygen. It is believed that ultra-violet light causes ionisation, and this may explain its accelerating influence.[63]

Under certain conditions, however, increase of illumination may cause a retardation of dry of linseed oil. This is noticed with linoleate driers at temperatures of the order of 5° C.[64]

The presence of moisture in the atmosphere has a retarding influence on the speed of dry.[65] This effect is especially noticeable when varnishes are drying in the very dirty atmospheres of large cities under humid conditions. In London, for example, inhibition of dry has occurred under these conditions, even inside testing laboratories. Also the deposition of moisture on varnishes or enamels during drying, from very humid atmospheres at low temperatures, has been a frequent cause of trouble

on exposed buildings in the course of erection. In bad cases, the dry of enamels and varnishes has been retarded for days. A week after application, although films had dried quite substantially, they showed very appreciable surface tack. According to Wolff and Zeidler, humidity, under certain conditions, exerts a greater influence at higher temperatures than at lower ones.[64]

Properties of Driers and Metallic Soaps

Influence of Metal.—The catalytic effect of different metals varies considerably, and from time to time tables have been reproduced demonstrating these variations.

	Mackey and Ingle [66]	*Eibner and Pallauf*	*Fokin* [67]
1.	Cobalt	Cobalt	Cobalt
2.	Manganese	Manganese	Manganese
3.	Lead	Lead	Chromium
	Cerium	Cerium	
4.	Chromium	Iron	Nickel
5.	Iron	Copper	Iron
6.	Uranium	Nickel	Platinum
7.	Sodium	Vanadium	Palladium
8.	Silver	Chromium	Lead
9.	Zinc	Calcium	Calcium
10.	Mercury	Aluminium	Bismuth
11.	Aluminium	Cadmium	Barium
12.	—	Zinc	Mercury
13.	—	Tin	Uranium
14.	—	—	Copper
15.	—	—	Zinc

Using precipitated linoleates in raw linseed oil drying tests were conducted by Datta and Das with cobalt, manganese, lead and iron driers at 25° C. and 60–70 per cent humidity. Cobalt (0·05 per cent) dried in two hours, manganese (0·08 per cent) in five hours, lead (0·58 per cent) in seventeen hours, and iron (0·41 per cent) in twenty-eight hours.[68] At more elevated temperatures (100°–150°) the order of activity of cobalt, manganese and then lead, remains unchanged.[69] Based on experiments with cobalt, difference in valency of the drying salt is stated to have little influence on the drying of linseed oil. Better drying is claimed if the varnishes or oils are allowed to age for some time after the addition of drier, in spite of the fact that some drier may be out of the sphere of action because of deposition. The better dry obtained is explained by an improvement in dispersion.[70] Krumbhaar, however, asserts that lead, cobalt and manganese are the best driers in the condition of highest valency.[59]

Combinations of Driers.—Much work has been conducted on the value of combinations of driers, and it is generally accepted that scientific blends are preferable to individual metals. There has not been complete unanimity of opinion concerning the relative effectiveness of certain combinations, but this is not surprising, for in evaluating drying properties many factors have an important bearing on the ultimate result.

The difficulty for different workers to reproduce identical experimental conditions, and the tendency to make deductions without due consideration for other variables, has led to much confusion in the assessment of results generally.

Combinations of driers are used not only to attain maximum speed of dry, but often to modify or eliminate unsatisfactory characteristics of certain individual driers.

The results of Winiker show that the ratio of the components of a combination varies with the total metal concentration. When the metal concentration is 0·6 per cent., lead and manganese should be used in the ratio of $7\frac{1}{3} : 1$ respectively, lead and cobalt in ratio of 5 : 1, and lead, manganese and cobalt in the ratio $9\frac{5}{8} : 1 : 1\frac{7}{8}$. At 0·3 per cent metal concentration, the lead, manganese and cobalt mixture gives two optimum ratios: $9\frac{5}{8} : 1 : 1\frac{7}{8}$ and $9\frac{5}{8} : 1\frac{7}{8} : 1$, the ratio for lead and manganese or for lead and cobalt remaining as for 0·6 per cent concentration. At lower metal concentrations, however (0·2 per cent), the lead-manganese combination is adjusted to $11\frac{1}{2} : 1$, the lead-cobalt to 5 : 1, and the lead, manganese and cobalt to 5 : 1 : 1.

It is also apparent that a combination of lead, cobalt and manganese has superior drying properties at all metal concentrations.[71] In obtaining the above results, Winiker used solutions of fused resinates in white spirit.

Datta and Das (*loc. cit.*) conducted experiments on combinations of driers under the conditions already described, and have recorded the following conclusions. Combinations of iron and lead or of cobalt and manganese were no better than the individual metals. Drying efficiency was increased 2·6 times with manganese-iron, 4·4 times with manganese-lead, 6·3 times with cobalt-lead and 6·6 times with cobalt-iron. The most efficient drying combination of all was a mixture of cobalt-lead-iron. A mixture of cobalt-lead-manganese-iron was next in order of efficiency.

The most common combinations of driers are, lead-cobalt, lead-manganese, lead - cobalt - manganese, cerium - cobalt and zinc-cobalt. Kiselev and Norina suggest mixtures of manganese-calcium-cobalt or manganese-calcium-lead as efficient combinations for paints.[72]

Drying Characteristics of Metals.—Drying metals do not all behave similarly in their effect on drying oils. Thus, for example, cobalt, manganese and iron all tend to promote rapid drying at the surface of the film, whilst lead, cerium, calcium, copper and zinc favour "through drying." It is not easy to explain why these metals behave differently, but at least two facts are available. It is always the metals which promote the most rapid drying which exhibit pronounced surface oxidation, as revealed by rivelling. According to Bassett, lead reduces the surface tension of linseed oil, but cobalt and manganese both increase it. Zinc is also stated to lower the surface tension.[73] It is reported that cerium gives stronger films than those obtained with lead, cobalt or manganese.[28]

Cobalt gives much harder films than those obtained with lead.[74]

Because drying metals behave differently and because in some circumstances certain characteristics are objectionable, combinations are used. Thus lead or cerium is used with cobalt or manganese to reduce the rivelling tendency of these powerful driers. Zinc and copper are also introduced in stoving finishes with the same object.

It is interesting to note that admixture of one drier with another does not always promote the catalytic power of the former. Results obtained by Flatt show that sometimes retardation of dry occurs. Using a blend of manganese and cobalt in the ratio of 1 : 3, the drying time was seventeen hours, but by increasing the ratio to 1 : 2 the drying time was eighteen hours. When the ratio of manganese to cobalt was 1 : 1 the time required was nineteen hours, and when the ratio was increased to 3 : 2 the drying time also increased to twenty hours. Therefore, the effect of increasing the amount of manganese in a manganese-cobalt mixture may result in a retardation of dry.[75] The ratio of metals in a drier combination may effect durability. Thus, in paints a lead-manganese ratio of 4 : 1 is better than 8 : 1.[76]

Optimum Amounts of Individual Driers.—Some controversy exists concerning the optimum amounts of individual driers. Weger gives 0·25 per cent for manganese. Curwen suggests that the optimum amount for lead is 0·65 per cent, and for manganese or cobalt 0·05 per cent.[77] Bassett (*loc. cit.*) suggests different optimum amounts according to the drying oil used. Thus, for tung oil, 0·26 per cent of lead is required and 0·03 per cent for manganese. For linseed oil the amounts are substantially increased to 1 per cent for lead, 0·1 per cent for manganese, and 0·04 per cent for cobalt. Wolff and Zeidler also give 0·1 per cent as the optimum amount for manganese.[64] For lead-manganese mixtures the amounts are 0·5 per cent lead and 0·1 per cent manganese.[78] Wolff and Zeidler suggest 6 : 1 as the optimum ratio for lead and manganese.

There is no doubt that the optimum amounts of drier for different types of varnish and media vary considerably. Manganese does not appear to be very effective in alkyds,[73] whereas zinc with special stoving types of this resin is particularly effective. Manganese driers are especially favoured for bituminous finishes of the stoving type.

In ordinary air-drying varnishes a good basis for formulation is to begin with 0·5 to 1·0 per cent lead, 0·04 per cent cobalt and 0·1 per cent manganese, wherever these metals are used, calculated on the finished varnish. It will then usually be necessary only to make minor adjustments to obtain satisfactory results.

Effect of Excess Driers.—The effect of excess driers on a varnish is not generally established. It has been handed down for years that excessive driers produce inferior durability, and it is stated that durability varies inversely as the cobalt content,[74] but this is not always the case, for experiments conducted by the author on natural copal varnishes revealed no diminution in durability with increasing cobalt content. However, as Knauss suggests, cobalt is the only drier likely to effect durability.[79]

Lead up to 1·5 per cent and manganese up to 0·4 per cent have no effect on durability.[74] Copper has no effect on durability.[80]

It is believed by some, with experimental backing, that excess of drier causes a retardation of drying, but it is probably safer to hold the view that beyond a certain amount, further increases of drier show no advantage.[75] There has been a tendency to exaggerate the retarding effect of excessive driers.

Influence of Acid Radical.—There is no doubt that the acid radical of a drying or other metallic soap exerts important influences on the properties of the soaps. Condition of the soap varies considerably with acid radical, for example, lead resinate is a hard resinous material, whilst the linoleate and naphthenate are comparatively soft and sticky. Generally, resinates of all metals are much harder than the corresponding linoleates, tungates, oleates or naphthenates. Acid radicals also influence the compatibility of the soaps with oils and hydrocarbons, and also the stability of the resultant solutions. Certain acid radicals stimulate the catalytic activity of metals, whilst others influence the drier such that it is more susceptible to variations of prevailing conditions.

Comparisons have been made of linoleates, resinates, and naphthenates. Lead and manganese naphthenates are claimed to have superior drying properties to the resinates or linoleates of these metals, which are similar. Cobalt resinate is superior to the linoleate, with cobalt naphthenate inferior to both. The same workers have made the interesting discovery that mineral spirits stimulate the drying activity of certain types of drier. It is observed with manganese resinate and linoleate and with lead and cobalt naphthenates.[81]

Gray states that improved dry is obtained with naphthenates, and points out that after a short induction period which is observed with cobalt, lead and manganese naphthenates, a distinct acceleration of drying takes place.[82] Knauss states that naphthenates exhibit improved drying properties only when the relative humidity is above 25. Resinates are sometimes better than naphthenates at lower humidites.[83]

Wolff and Zeidler have compared a mixture of lead and manganese linoleates with a mixture of lead and manganese resinates when used as driers in lithopone-linseed oil paints. The resinates are more susceptible to temperature variations and other influences than the linoleates.[76] The same workers have reported that for linoleate driers, the temperature coefficient of drying time remains constant for various lead-manganese ratios. Considerable variation is observed, however, with resinates, the temperature coefficient decreasing as the proportion of lead increases.[64]

With linseed oil at 98·5°, the linoleates of manganese and cobalt give the same induction period as the corresponding oleates. These four soaps all give a shorter induction period than lead linoleate.[84]

The differences in behaviour during drying which occur between naphthenates on the one hand and linoleates and resinates on the other, may be attributed to the fact that the latter are both unsaturated and

subject to oxidation themselves, whereas the former is completely saturated. Manganese tungate is stated to have excellent drying properties. Wang claims that it is a better drier than other tungates.[85]

There is no difference between naphthenates and linoleates in their effect on durability.[74]

Naphthenates have many advantages over linoleates or resinates. They have substantially higher metal contents, and this means that economies are effected in transportation and handling. Moreover, it is not necessary to make such large additions of drier to obtain a given amount of metal in the varnish. Naphthenates give more stable solutions both in oil and in hydrocarbons. They dissolve more readily and remain in solution without precipitation. With lead naphthenate in oils, however, some precipitation does occur ultimately, although it is not so pronounced as with linoleates or resinates. According to Knauss, when lead linoleate, resinate or naphthenate is added to raw linseed oil the antioxygens of the oil are precipitated, and a difference in behaviour is noticed between naphthenate and the other two soaps. When more soap is added than is necessary to precipitate the antioxygens it tends to remain in solution if a naphthenate, but deposits more rapidly if linoleate or resinate.[86]

Klebsattel points out that naphthenates are much more resistant to oxidation than linoleates and resinates which tend to skin during storage. The latter also produce after-yellowing.[87]

Curwen states that with naphthenates risk of spontaneous combustion during storage is eliminated. Resinates of cobalt and cerium are liable to exhibit this unpleasant property, but there is said to be no danger with the corresponding naphthenates.[88]

Naphthenates have lower melting-points than the corresponding resinates, and this enables solutions to be obtained at lower temperatures with the consequent improvement in colour.

Bryson (*loc. cit.*) records that naphthenates show less tendency to be poisoned than other drying compounds, which includes the resinates and linoleates.[89]

Absorption of Drier.—Pigments sometimes exert a profound influence on driers. The phenomenon of adsorption of driers with loss of drying power is due to adsorption of drier by the pigment. The pigments with large specific surface areas are the ones which show the greatest inhibition of dry,[89] and these include carbon blacks, siennas, umbers, iron oxide, madder lake, zinc oxide and titanium oxide. The tendency to adsorption varies with the valency of the drying metal, thus trivalent cobalt is more readily adsorbed than the monovalent form. It is emphasised by Bryson that oils also tend to adsorb driers.

Pigments may act as oxidising or reducing agents. Carbon black, iron oxide and titanium dioxide oxidise driers. Calcium carbonate, barium sulphate, zinc oxide and white lead reduce them.[70]

The loss of drying power of pigmented media should not be attributed entirely to adsorption by pigment. It may be due to precipitation of drier.[90]

There are several methods for preventing loss of drying power due to adsorption of drier. Excess drier may be added initially and the paint or enamel allowed to stand until the adsorption is complete, sufficient drier being left to give normal drying.[90] Alternatively, substances such as zinc naphthenate and oxides of lead, magnesium or calcium, may be added initially to satisfy adsorption and the true driers are added subsequently. Sometimes a repetition of the grinding process will regenerate a loss of drying power due to pigment adsorption.[91]

Lead Soaps

Lead soaps are present in almost every type of varnish, paint, enamel or stoving finish. When they are added in the form of soaps, the linoleate, resinate or naphthenate is used. Of these the linoleate and the naphthenate are the most popular, with the naphthenate fast replacing the linoleate.

Fused lead linoleate is a soft cheesy material varying in colour from light to dark brown depending upon the care taken in manufacture. Precipitated lead linoleate is usually paler in colour than the fused linoleate. In bulk both types of linoleate appear cloudy. Lead linoleates are soluble in white spirit, but it is almost impossible to obtain a clear solution. This is explained by the presence of lead soaps of saturated acids which are insoluble. Solutions of lead linoleate in white spirit have poor keeping qualities. They deposit foots very rapidly. Not only is this very wasteful but it is impossible to state with certainty the metal content of the solution at any given time. This is one factor which has done more than any other to cause substitution by naphthenate. Although lead naphthenate is more expensive initially than the linoleate, it has been found that after making allowances for the lead wasted with the latter, and taking into consideration labour involved in cleaning storage tanks, etc., it is not only preferable but cheaper to use the naphthenate.

A comparison of lead linoleate obtained by precipitation, with the compound formed by reaction of litharge with linseed oil, reveals no advantage in dry to be obtained with the latter, in spite of a popular conception to the contrary.[92] Sabin, in fact, asserts that the litharge-linseed oil complex by comparison with precipitated linoleate causes rapid drying and rivelling.[93] If the litharge-linseed oil complex is dissolved in hydrocarbon it yields a clear solution which remains thus for long periods, only becoming cloudy gradually. On the other hand, it is impossible to obtain a clear solution with the precipitated linoleate. On adding the two types of terebine to linseed oil the precipitated linoleate gives an almost immediate white precipitate, but the litharge-linseed oil complex remains clear for twenty-four hours.

Lead naphthenate is a light brown sticky solid which melts at about 100° C. It dissolves easily in white spirit to give a clear solution which should show no tendency to deposit any sediment. With very carefully prepared lead naphthenate very pale straw coloured terebines are possible.

Lead resinate has the appearance of a brownish friable resin. The precipitated form is sometimes available as a pale yellow powder.

Lead oleate has enjoyed some popularity as a drier in the past, but it is little used nowadays. If it is made from pure oleic acid it should offer definite advantages over the ordinary linoleate. It would be comprised entirely of the lead salt of unsaturated acid, and this is much more soluble in hydrocarbons than lead salts of saturated acids. Lead oleate should yield, therefore, terebines with less tendency to separate than those based on linoleate, which has a certain amount of saturated acid present.

One of the major defects of lead driers is their tendency to precipitate from varnishes. In natural copal varnishes the precipitate is usually ascribed to saturated lead soaps such as lead stearate. In alkyds, however, the precipitate is believed to be lead phthalate produced by interaction of the lead drier and the free phthalic acid of the resin.[94]

Separation of driers from Japan driers has been attributed to flocculation or crystallisation of the drier from a supersaturated solution, or it may be due to precipitation of insoluble salts of oxidised fatty acids.[95] Turbidity of varnishes containing lead driers may not always be due to precipitation of insoluble lead soaps. Knauss explains that the turbidity of tung oil-ester gum varnishes may be due to coagulation of the colloidal varnish in the presence of lead naphthenate. The tendency to coagulation disappears with increase of acidity.[96]

The tendency of lead driers to precipitate from alkyds is lessened if fractional percentages of benzoic acid are added. The remedy is, however, only temporary. Rosin may be added to varnishes containing linoleate driers to prevent precipitation, but according to Sabin this procedure is not recommended, for the abietic acid of the rosin substitutes the fatty acids of the drying soap and other disadvantages may be introduced.[93]

Experiments have been conducted on the effect of lead driers on the properties of an ester gum-tung oil-linseed oil varnish. The chief advantage gained by using lead is improved wetting properties, but disadvantages are introduced also. These include reduction of water and chemical resistance, loss of durability and flow, and a tendency to promote settling.[97] Further experiments on varnishes containing tung oil-linseed oil, with pure and modified phenolics, congo, and ester gum, showed that lead gave improved drying in enamels, but increased floating and flooding of chrome greens.[98]

Other lead soaps which are used to a small extent in varnish manufacture are the palmitate and stearate. These are usually available as white waxy lumps or as powder. Lead palmitate has a melting-point of 112·3° C., and the stearate 115·7° C. They are soluble in hot vegetable oils, alcohols, chloroform and hydrocarbons but separate on cooling. They are quite insoluble in cold alcohol.

Cobalt Soaps

The most popular cobalt soap used as a drier is cobalt linoleate, with the naphthenate as the next in importance. A pure cobalt linoleate is a very stiff violet substance. It is not much used in this highly concentrated form because of some difficulty in dispersion, but in the diluted form, the diluents being linseed oil, linseed oil fatty acids or mineral spirits. Cobalt linoleate solutions, which are very easily dispersed, contain 4 to 6 per cent metal. Because of the natural dark colour of this drier and the very small quantities which are used, it is not usual to pay much attention to achieving improvements in colour. Because of its ease of manufacture from cobalt hydrate, its ready solubility when molten, and its stability, there has not been the same tendency to substitute it by naphthenate as with other metals. Cobalt was first made and used as the resinate, then as the oleate, and now as the linoleate and naphthenate.

Cobalt naphthenate is a harder product than the linoleate, being resinous in character, and it can be shattered in fragments by sharp blows. It has a melting-point of 130° C. approximately.

Cobalt resinate is a violet coloured friable resinous material. It is usually made containing about 2–3 per cent metal. Cobalt (ous) oleate is a brown amorphous powder soluble in alcohol, benzene, ether and oils.

In modified phenol formaldehyde-tung oil varnishes the presence of cobalt and manganese driers aids in maintaining lead driers in solution.[99]

Cobalt is not always a satisfactory drier for use with iron blues, but it is claimed to be the best drier for dehydrated castor oil.[100]

In the presence of turpentine the violet or reddish-blue colour of cobalt driers is changed to dark green.

Solutions of cobalt naphthenate in mineral spirits sometimes have a tendency to gel on storage, and this is overcome by additions of acidic stabilisers, or incorporation of a few per cent of butyl alcohol in the mineral spirits.

Cobalt causes considerable darkening of films which are stoved, and in such varnishes the cobalt should be kept at a minimum if absence of darkening is important. Similarly, cobalt causes a considerable reduction in the water resistance of air-dried films.

Manganese Soaps

Manganese is used in the form of linoleate, naphthenate and resinate. The fused linoleate is a dark reddish-brown tough solid in contrast with the precipitated linoleate which has a pale orange colour. In producing pale terebines including manganese, it is necessary to use the precipitated soap.

Manganese naphthenate is similar to the fused linoleate in appearance but is tougher. It has a melting-point of approximately 130° C. The resinate is a brown friable resin.

Manganese naphthenate is not easy to melt and thin with mineral

spirits. Addition of fluxes such as plasticisers or acidic substances are an advantage. Solutions of manganese naphthenate in mineral spirits have a more pronounced tendency to gel than similar cobalt solutions, and they yield solutions with inconveniently high viscosities. The addition of 5 per cent of butyl alcohol to the mineral spirits not only improves the stability of the solution but causes substantial reduction in viscosity also. Like cobalt, films containing manganese darken considerably on stoving.

Iron Soaps

Iron driers may be classified among the little used driers. In some old formulæ for asphaltum finishes, both air drying and stoving, prussian blue is used as a drier and is cooked into the oils, etc., in the usual way as with other inorganic metallic compounds.

Other iron compounds which are used include the linoleate and the naphthenate. Both soaps have intense reddish-brown colours. The colour is sometimes exploited in gold stoving varnishes. The linoleate is a soft pasty substance whereas the naphthenate is stiffer.

Iron oleate is a brownish-red substance soluble in alcohol, ether and hydrocarbons.

Cerium Soaps

During recent years a certain interest has been apparent in the use of cerium as a substitute for lead. Since it has similar drying characteristics to lead it has replaced it to some extent where it has been considered essential to eliminate all tendency to precipitation during storage. Cerium soaps are much more soluble than lead soaps in oils and varnish compositions generally. They have replaced lead, with some success, in air-drying alkyd varnishes. Although all tendency to cause turbidity is eliminated, the presence of cerium causes considerable darkening of the varnish both in the original varnish and as a film. This has militated to some extent against its use generally.

Cerium naphthenate is the only cerium soap that is used to any extent. It is a soft light brown solid not unlike lead naphthenate in appearance.

When required as a terebine it is best dissolved in aromatic hydrocarbons like naphtha or xylol, in preference to mineral spirits in which it is sometimes unstable.

Vanadium Soaps

Soluble vanadium soaps have good drying properties. They are claimed to be only slightly inferior to cobalt. The chief disadvantages which prevent their general use are cost and the fact that they are dark in colour.

Zinc Soaps

Zinc soaps are becoming increasingly popular in varnish manufacture, and this is due, primarily, to the introduction of various zinc resinates. Zinc naphthenate is used in fair quantities, and zinc stearate and palmitate are used in lesser amounts for special purposes. The linoleate is rarely encountered.

Zinc resinates have appeared on the market as pale brownish-yellow resins under such names as Zinio, Zirex, Zinar, Zitro, etc. Some of these soaps contain abnormally high percentages of zinc. Most of the zinc resinates have very good solubility or compatibility. They are soluble, both in aliphatic and aromatic hydrocarbons, turpentine, esters and ethers. They are insoluble in alcohol. Zinc resinates are compatible with the usual drying oils and with most natural and synthetic resins.

In making cold solutions of zinc resinate in white spirit, dissolution is facilitated if a small amount of water (0·2–0·3 per cent calculated on the resinate) is added to the white spirit first. The presence of the water also greatly reduces the viscosity of the resultant solutions. Zinc resinate gives better wetting properties than lead in enamels, and other advantages are less tendency to rivel or skin, improved flow and gloss, and less settling. Lead soaps give superior initial dry, but both lead and zinc reach the hard dry condition simultaneously.

Zinc resinate is especially recommended for inducing "through dry" in alkyds. It may be used as a resin, and in this rôle it can substitute ester gum with advantage where durability is concerned, or it can partly replace modified phenolic resin without loss of durability. Edelstein claims further that when zinc resinate is used, linseed, perilla or fish oils may substitute tung oil without serious loss of durability.[102] Short oil zinc resinate-blown linseed oil combinations make excellent gold-sizes.

The zinc resinate (Zirex) with its abnormal metallic content (9·6 per cent zinc) is able to react with acidic substances because of its basicity. Thus it can be reacted with drying oil fatty acids or rosin. Basic zinc resinate is claimed also to prevent turbidity in phenolic varnishes.

Although, generally, it is acidic substances which retard gelation of tung oil, this result is obtained with basic zinc resinate also.[103] Zinc resinates are also good gel dispersers.

Zinc naphthenate is a pale brown, soft, sticky, easily fusible substance which dissolves rapidly in hydrocarbons. It is said by Curwen to precipitate from high acid value vegetable oils.[104]

Rollins has studied the effect of driers on Californian sardine oils. A blend of cobalt and zinc caused less discoloration of the film than a blend of lead and manganese. Using a combination of cobalt and zinc, the most satisfactory amounts are given as 0·1 per cent cobalt with 0·05 per cent zinc. The function of the zinc is to toughen the film.[105]

Zinc oiticicate, the zinc salt obtained from the fatty acids of oiticica oil, has been suggested[124] as a better flatting agent than aluminium

stearate. Other metallic oiticicates can be used, e.g. the calcium, magnesium and aluminium salts but they are not so easy to manipulate as the zinc soap.

There are three methods of dispersing the zinc oiticicate. The first consists in melting equal parts of the soap and a selected hard resin, separately, and adding the molten soap to the resin below 300° F. The mixture is cooked for an hour at 280° F. and allowed to cool or thinned. In the latter case, a mixed solvent is used consisting of Varnolene (3 pts.) and solvent naphtha (1 pt.). The products are used as flatting bases.

The second method involves thinning the molten zinc soap with a varnish thinner from which it precipitates on cooling, and running the mixture through a water-cooled mill. The soap is said to precipitate in colloidal form. Alternatively, the cool rough dispersion in Varnolene is ground in a ball mill at a low temperature.

The advantages of zinc oiticicate in flat varnishes over other metallic soaps are easier manipulation, absence of cheesiness in films, permanent dispersion without settlement and only slight bodying tendency.

Aluminium Soaps

The outstanding property of aluminium soaps is their tendency to gel. Whilst it has been recorded that aluminium can perform the function of a drier it is rare that use is made of this property. Both Gardner and Morrell [106] have confirmed the drying properties of aluminium soaps, the latter with aluminium resinate. It is said that aluminium has better drying properties than lead. Aluminium naphthenate and stearate are the most important soaps in regular use. Aluminium naphthenate is a pale brown jelly-like or rubbery substance with a tendency to crumble if subjected to force. It does not fuse readily, and is difficult to get into solution in hydrocarbons, but once a solution is obtained it is fairly stable if the percentage of soap is not too high. As with other soaps where difficulty is encountered in effecting solution, the addition of a little butyl alcohol is a distinct advantage.

Aluminium stearate is available as a white powder, in many different grades with different properties. These soaps are prepared to suit the individual requirements of certain processes. The data (page 390) abstracted from the technical literature of a manufacturer * is indicative of the variation in properties which it is possible to obtain.

Aromatic hydrocarbons are the best dispersing agents for aluminium stearate, being superior to aliphatic hydrocarbons, esters, alcohols or ketones.[107] For some purposes it is necessary to grind aluminium stearate in a solvent or thinner. For this purpose a blend of equal parts of toluol and butyl acetate is suggested. Licata states that where a mixture of gel producing liquid with suspension producing liquid is used, the suspension producing liquid exerts the greater influence. Toluol is used with esters or alcohols.[108] Production of heat should be avoided

* Messrs. A. Boake Roberts & Co. Ltd., Stratford, London.

during grinding as this may cause gelation. Aluminium stearate gels are transparent. Ruemele chooses aluminium stearates of high acidity for use with highly polymerised oil varnishes, and for cellulose lacquers stearates with low ash are preferred.[109]

Grade of Al. Stearate.	Melting-Point (approx.).	Gelling range		Nature of Gels, etc.
		in Xylene.	in Mineral Oil.	
Higel 1 .	160° C.	55°–60° C.	100°–105° C.	Clear firm jelly.
Higel 2 .	140° C.	50°–55° C.	95°–100° C.	Less rigid jelly than Higel 1.
Higel 11 .	165° C.	60°–65° C.	105°–110° C.	Rigid, elastic jelly.
Higel 22 .	160° C.	55°–60° C.	100°–105° C.	Rigid jelly.
Higel LM .	115° C.	65°–70° C.	100°–105° C.	Soft, inelastic jelly.
Nogel .	—	—	—	Does not gel: forms suspensions.

Aluminium palmitate is used for similar purposes to the stearate. Commercial aluminium oleate is a yellow, tacky, semi-solid mass. It is easily soluble in benzene on warming, but insoluble in alcohol.

Calcium Soaps

The most important calcium soap is the resinate. It is a brittle resin, and if carefully prepared should be of a pale straw colour. Most limed rosins are slightly opalescent. The soap is readily soluble in aliphatic, or aromatic hydrocarbons and drying oils, and has excellent compatibility with most common oil and synthetic varnish constituents. It has a higher melting-point than rosin. Although its acidity is considerably less than that of rosin, it is not possible to obtain a limed rosin which is almost neutral. Often the acidity is high enough to cause feeding with basic pigments.

Calcium resinate prepared from natural wood rosin gives solutions of lower viscosity than similar resinates from gum rosin. Specially treated wood rosins are made, however, which yield calcium resinates of higher melting-point, higher solution viscosity, and paler colour, than gum rosin resinates.

Calcium naphthenate is a soft, pale straw substance of good solubility. The linoleate is a white amorphous powder soluble in ether and alcohol. The palmitate is also a white powder, but is only slightly soluble in alcohol.

Chromium Soaps

These are but little used. The naphthenate is available as a soft, sticky, purple coloured substance.

Copper Soaps

The naphthenate is by far the most important of the copper soaps. It is a very stiff, dark green material which just fractures when subjected to sharp blows. If a sharp blade is thrust into it the incision appears white. The soap is not always smooth in appearance, but sometimes appears rough and seedy as if it contained some insoluble matter in suspension. Its dark green colour may affect whites and tinted white enamels. It is soluble in aliphatic hydrocarbons, and it is in this form in which it is mostly used.

Copper naphthenate is used in conjunction with the more powerful driers to prevent rivelling, especially in stoved films. Copper sometimes has a definite retarding influence on the dry which is more pronounced than that of zinc. To minimise rivelling, Mickler suggests the use of 0·05 per cent of copper in the form of naphthenate, and claims that up to 0·3 per cent of metal does not inhibit dry.[80]

Copper naphthenate is said to be much more effective in inducing gloss in enamels than zinc naphthenate. It is used also to eliminate skinning and webbing.

Copper palmitate is a greenish-blue powder with a melting-point of 120° C., and is slightly soluble in alcohol. The stearate is a light blue amorphous powder with a melting-point of 125° C., soluble in benzene, turpentine, chloroform and ether.

Zirconium Soaps

These, as yet, are of little more than academic interest only. The naphthenate is a heavy amber liquid with no real drying properties.

Magnesium Soaps

The oleate is a yellowish powder soluble in linseed oil and slightly soluble in ether and alcohol. The melting-points of the palmitate and stearate are 121·5° C. and 132° C., respectively.

Silver Soaps

The palmitate has a melting-point of 209° C. and the stearate 205° C.

The Uses of Driers and Metallic Soaps

Metallic soaps probably have a more widespread application than any other raw materials. Apart from their use as driers, an aspect which has been considered already, they are used also for the following purposes.

Waterproofing Agents.—They are used to a considerable extent in waterproofing compositions, and it is generally the soaps of saturated acids like palmitic and stearic acids which are selected for this purpose. The most popular waterproofing soaps are aluminium stearate and palmitate. Other soaps used for waterproofing include the salts of titanium, zirconium and thorium.[40] Cerium naphthenate is claimed to have good

waterproofing properties, and is used in spar varnishes and in impregnating compositions for ropes and sails.[28] Interaction between pigments and the free fatty acids of a paint medium may result in the formation of soaps which give improved water resistance.[110] Metallic soaps are incorporated in many cellulosic and synthetic compositions which provide water resistant finishes for all manner of surfaces, including cellophane, paper, etc. Thus a washable finish for wallpaper comprises a cellulose derivative, and zinc or aluminium stearate.[111] The soaps may be used in conjunction with wax.

Matting Agents.—Due to the comparative insolubility of the metallic soaps of saturated acids, these soaps are valuable matting agents. This property is exploited both in cellulose and oil base products. Soaps used for this purpose are lead stearate, zinc oiticicate, aluminium stearate, palmitate, and the aluminium soap derived from a modified phenolic resin described by the name of Albertate. A flat varnish based on an oleoresinous varnish contains the calcium, magnesium, aluminium or zinc soap derived from the free fatty acids of Japan wax.[112]

Non-Settling Agents.—Metallic soaps are valuable non-settling agents. Their property of forming gels is effective in maintaining pigments in suspension. Aluminium stearate and naphthenate are often present in small amounts in paints, varnish paints, enamels and metal polishes for this purpose.

Penetration Inhibitors.—The tendency to form a gel structure is also a valuable property in the manufacture of printing inks and varnishes. In such products it is often essential for the film to remain on the surface of the paper with minimum penetration. The formation of the gel structure in the film aids in accomplishing this. Thus an over-printing varnish may be formulated on tung oil, linseed oil, and natural or synthetic resins. To this base is added aluminium stearate, or magnesium stearate, palmitate or oleate. In an example 15 parts of aluminium stearate are mixed with 305 parts of the oleoresinous portion of a varnish.[113]

Krumbhaar asserts that the soaps of magnesium, calcium and zirconium are preferable to those of aluminium, for with the latter the non-penetrating properties are apt to be temporary only, due to the flocculation of certain pigments.[114]

Basic aluminium soaps have been used also in non-penetrating paints.[115] A medium for printing ink is made from resin, mineral oil and metallic soaps.[116]

Although metallic soaps may confer certain valuable properties, they often produce defects simultaneously. The two commonest are inferior adhesion and loss of durability.

Wetting Agents.—The use of metallic soaps as wetting agents for pigments has been mentioned already. The naphthenates of zinc and lead have found application here.

Rot Proofing Agents.—Considerable quantities of copper and zinc naphthenates are used in rot-proofing solutions for the impregnation of

wood, fabric, fishing nets and jute bags. Of these two soaps copper is by far the most effective. The soaps are used as solutions in white spirit, distillate, paraffin, toluene or turpentine. Copper oleate was used originally for rot proofing, but is now almost completely replaced by the naphthenate. It has been suggested that the solubility of copper naphthenate can be reduced with advantage, if aluminium naphthenate or a similar water resistant compound is mixed with it.

Antifouling Agents.—Metallic soaps, especially those of copper, mercury, and arsenic are used in antifouling paints for ships' bottoms.

Emulsifying Agents.—Water soluble metallic soaps, derived from sodium, potassium and ammonium are valuable emulsifying agents.

Chalking Inhibitors.—Some soaps have been found to minimise or eliminate the chalking tendency of pigments like titanium dioxide, which exhibits this defect on exposure. Of the soaps recommended for this purpose, tin oleate and resinate, chromium oleate,[117] and zirconium naphthenate [28] are worthy of inclusion, although the value of zirconium naphthenate has not been definitely confirmed.

Other Uses.—Aluminium stearate and soaps of titanium, thorium and zirconium are used in the manufacture of lubricants.

Special applications of metallic soaps are in paint media or varnishes, where they sometimes replace resin. It has been mentioned already how the resinates of zinc and calcium can act as resin substitutes, but calcium naphthenate has been suggested to perform this rôle also. A solution of calcium naphthenate, one part, dissolved by heating in one part of linseed oil and thinned with three parts of benzine has been used as a varnish.[118] A paint medium is produced from a drying oil, resin, cobalt linoleate, manganese ricinoleate, and from the insoluble soaps of aluminium, iron and zinc. Paint media from sulphur treated oils frequently contain magnesium oleate.[119]

A floor varnish is formulated from linseed and tung oils, limed rosin, paraffin wax, zinc stearate and thinner.[120]

Among less important uses of metallic soaps is the addition of naphthenate (0·01 to 0·3 per cent) to cellulose acetate to render it less susceptible to discoloration by heat ; [121] the addition of 2–10 per cent of magnesium oleate, lead oleate, zinc laurate, zinc stearate with barium fluoride, or calcium stearate with zinc oxide, to a polyvinyl resin derived from hydrolised polyvinyl acetate, to improve the toughness ; [122] in paint removers to retard the evaporation of solvents and to provide a convenient viscosity ; in fillers and sealers for wood before the application of cellulose lacquers ; the acceleration of the polymerisation of linseed oil with aluminium naphthenate ; [123] and in the sizing of paper during paper manufacture where aluminium resinate is used.

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METALLIC CONTENTS OF DRIERS, SALTS AND SOAPS

Drier, Salt or Soap.	Formula.	M.Wt.	% Metal.
ALUMINIUM	Al	27·1	100·0
Aluminium—			
chloride	$Al_2Cl_6 . 12H_2O$	266·8	20·3
hydroxide	$Al_2(OH)_6$	156·0	34·7
nitrate	$Al(NO_3)_3 . 9H_2O$	375·3	7·2
oxide	Al_2O_3	102·0	53·0
sulphate	$Al_2(SO_4)_3$	342·2	15·8
	$Al_2(SO_4)_3 . 9H_2O$	504·3	10·8
	$Al_2(SO_4)_3 . 18H_2O$	666·6	8·1
acetate	$Al(CH_3COO)_3$	204·0	13·3
oleate	$Al(C_{18}H_{33}O_2)_3$	871·2	3·1
stearate	$Al(C_{18}H_{35}O_2)_3$	877·2	3·1
palmitate	$Al(C_{16}H_{31}O_2)_3$	793·1	3·4
linoleate			3·3
naphthenate			4·0
resinate			2·6
tungate			3·3
AMMONIA	NH_3	17·0	
"AMMONIUM"	NH_4	18·0	100·0
Ammonium—			
acetate	NH_4CH_3COO	77·1	23·4
bicarbonate	$NH_4 . HCO_3$	79·1	22·8
carbonate	$(NH_4)_2CO_3 . H_2O$	114·1	31·6
chloride	NH_4Cl	53·5	33·7
nitrate	NH_4NO_3	80·1	22·5
oxalate	$(NH_4)_2(COO)_2$	124·1	29·1
	$(NH_4)_2(COO)_2H_2O$	142·1	25·4
sulphate	$(NH_4)_2SO_4$	132·1	27·3
oleate	$NH_4 . C_{18}H_{33}O_2$	299·4	6·0
palmitate	$NH_4 . C_{16}H_{31}O_2$	273·4	6·6
stearate	$NH_4 . C_{18}H_{35}O_2$	301·4	6·0
linoleate			6·4
naphthenate			7·7
resinate			5·0
tungate			6·4
ANTIMONY	Sb	120·2	100·0
Antimony—			
trichloride	$SbCl_3$	226·6	53·0
pentachloride	$SbCl_5$	297·5	40·4
sulphate	$Sb_2(SO_4)_3$	528·6	45·5
trioxide	Sb_2O_3	288·4	83·3
pentoxide	Sb_2O_5	320·4	75·0
BARIUM	Ba	137·4	100·0
Barium—			
acetate	$Ba(CH_3COO)_2 . H_2O$	273·4	50·3
carbonate	$BaCO_3$	197·4	69·6
chloride	$BaCl_2$	208·3	66·0
	$BaCl_2 . 2H_2O$	244·3	56·2
hydroxide	$Ba(OH)_2 . 8H_2O$	315·5	43·5
oxide	BaO	153·4	89·5
nitrate	$Ba(NO_3)_2$	261·4	52·6
peroxide	BaO_2	169·4	81·1
oleate	$Ba(C_{18}H_{33}O_2)_2$	700·1	19·6
palmitate	$Ba(C_{16}H_{31}O_2)_2$	648·1	21·2
stearate	$Ba(C_{18}H_{35}O_2)_2$	704·1	19·5
linoleate			20·6

METALLIC CONTENTS OF DRIERS, SALTS AND SOAPS—*Continued*

Drier, Salt or Soap.	Formula.	M.Wt.	% Metal.
Barium—			
naphthenate			24·3
resinate			16·9
tungate			20·9
BISMUTH	Bi	209·0	100·0
Bismuth—			
hydroxide	$Bi(OH)_3$	260·0	80·4
nitrate	$Bi(NO_3)_3 . 5H_2O$	485·1	43·1
	$Bi(NO_3)_3 . 6H_2O$	503·1	41·6
pentoxide	Bi_2O_5	498·0	83·9
sulphate	$Bi_2(SO_4)_3$	706·2	59·2
trichloride	$BiCl_3$	315·4	66·3
trioxide	Bi_2O_3	466·0	89·7
oleate	$Bi(C_{18}H_{33}O_2)_3$	1053·2	19·9
palmitate	$Bi(C_{16}H_{31}O_2)_3$	975·0	21·5
stearate	$Bi(C_{18}H_{35}O_2)_3$	1059·2	19·7
linoleate			20·8
naphthenate			24·5
resinate			17·1
tungate			21·0
CADMIUM	Cd	112·4	100·0
Cadmium—			
carbonate	$CdCO_3$	172·4	65·2
chloride	$CdCl_2 . 2H_2O$	219·4	51·2
	$CdCl_2$	183·3	61·3
	$CdCl_2 . 2\frac{1}{2}H_2O$	228·4	49·3
hydroxide	$Cd(OH)_2$	146·4	76·6
nitrate	$Cd(NO_3)_2 4H_2O$	308·5	36·5
oxide	CdO	128·4	87·5
acetate	$Cd(CH_3COO)_2 2H_2O$	266·5	42·1
sulphate	$3CdSO_4 . 8H_2O$	769·5	43·8
	$CdSO_4 . 4H_2O$	280·5	40·1
	$CdSO_4$	208·5	53·9
oleate	$Cd(C_{18}H_{33}O_2)_2$	675·1	16·6
palmitate	$Cd(C_{16}H_{31}O_2)_2$	623·1	18·1
stearate	$Cd(C_{18}H_{35}O_2)_2$	679·1	16·5
linoleate			17·5
naphthenate			20·7
resinate			14·2
tungate			17·6
CALCIUM	Ca	40·1	100·0
Calcium—			
acetate	$Ca(CH_3COO)_2$	158·1	25·3
	$Ca(CH_3COO)_2 H_2O$	176·1	22·8
carbonate	$CaCO_3$	100·1	40·1
chloride	$CaCl_2 . H_2O$	129·0	31·0
	$CaCl_2 . 6H_2O$	219·1	18·3
	$CaCl_2 . 2H_2O$	147·0	27·2
	$CaCl_2$	111·0	36·1
hydroxide	$Ca(OH)_2$	74·1	54·1
nitrate	$Ca(NO_3)_2$	164·1	24·4
	$Ca(NO_3)_2 3H_2O$	218·1	18·3
	$Ca(NO_3)_2 4H_2O$	236·1	17·0
oxide	CaO	56·1	71·5
oxalate	$Ca(COO)_2$	128·1	31·3
sulphate	$CaSO_4$	136·1	29·4
	$CaSO_4 . 2H_2O$	172·2	23·3

METALLIC CONTENTS OF DRIERS, SALTS AND SOAPS—*Continued.*

Drier, Salt or Soap.	Formula.	M.Wt.	% Metal.
Calcium—			
oleate	$Ca(C_{18}H_{33}O_2)_2$	602·8	6·6
palmitate	$Ca(C_{16}H_{31}O_2)_2$	550·7	7·3
stearate	$Ca(C_{18}H_{35}O_2)_2$	606·8	6·6
linoleate			7·0
naphthenate			8·5
resinate			5·9
tungate			7·1
CERIUM	Ce	140·2	100·0
Cerium—			
sesquioxide	Ce_2O_3	328·5	85·4
Cerous—			
chloride	Ce_2Cl_6	493·3	56·9
carbonate	$Ce_2(CO_3)_3 5H_2O$	550·6	50·9
sulphate	$Ce_2(SO_4)_3$	568·7	49·3
	$Ce_2(SO_4)_3 . 4H_2O$	640·5	43·8
	$Ce_2(SO_4)_3 . 8H_2O$	712·7	39·6
	$Ce_2(SO_4)_3 9H_2O$	730·6	38·4
Ceric sulphate	$Ce(SO_4)_2 . 4H_2O$	404·4	34·6
Cerous—			
acetate	$Ce(CH_3COO)_3 . 1\frac{1}{2}H_2O$	344·2	40·8
oxalate	$Ce_2(COO)_6$	544·5	51·5
	$Ce_2(COO)_6 . 9H_2O$	706·4	39·8
oleate	$Ce(C_{18}H_{33}O_2)_3$	984·4	14·2
palmitate	$Ce(C_{16}H_{31}O_2)_3$	906·3	15·5
stearate	$Ce(C_{18}H_{35}O_2)_3$	988·4	14·2
linoleate			15·0
naphthenate			17·8
resinate			12·1
tungate			15·1
CHROMIUM	Cr	52·0	100·0
Chromic acetate	$Cr(CH_3COO)_3 . H_2O$	247·1	21·1
Chromium—			
sesquioxide	Cr_2O_3	152·0	68·4
trioxide	CrO_3	100·0	52·0
Chromic—			
chloride	Cr_2Cl_6	317·8	32·8
	$CrCl_3 . 10H_2O$	338·5	15·4
nitrate	$Cr(NO_3)_3 9H_2O$	400·2	13·0
	$Cr(NO_3)_3 . 7\frac{1}{2}H_2O$	373·2	13·9
sulphate	$Cr_2(SO_4)_3$	392·2	26·5
	$Cr_2(SO_4)_3 5H_2O$	482·3	21·6
	$Cr_2(SO_4)_3 . 15H_2O$	662·4	15·7
	$Cr_2(SO_4)_3 18H_2O$	716·4	14·5
Chromous—			
chloride	$CrCl_2$	122·9	42·3
sulphate	$CrSO_4 . 7H_2O$	274·3	19·0
Chromic—			
oleate	$Cr(C_{18}H_{33}O_2)_3$	896·1	5·8
palmitate	$Cr(C_{16}H_{31}O_2)_3$	818·0	6·4
stearate	$Cr(C_{18}H_{35}O_2)_3$	902·1	5·8
linoleate			6·1
naphthenate			7·4
resinate			4·9
tungate			6·2

METALLIC CONTENTS OF DRIERS, SALTS AND SOAPS—*Continued*

Drier, Salt or Soap.	Formula.	M.Wt.	% Metal.
COBALT	Co	59·0	100·0
Cobalt—			
acetate	$Co(CH_3COO)_2$	177·0	33·4
	$Co(CH_3COO)_2 . 4H_2O$	249·0	23·5
carbonate	$CoCO_3$	119·0	49·5
	$4CoCO_3 . Co(OH)_2 . 5H_2O$	659·0	44·7
chloride	$CoCl_2$	129·9	45·4
	$CoCl_2 . 6H_2O$	238·0	24·8
	$CoCl_2 . 2H_2O$	165·9	35·6
hydroxide	$Co(OH)_2$	93·0	63·4
nitrate	$Co(NO_3)_2 6H_2O$	291·1	20·2
oxide	CoO	75·0	78·7
	Co_2O_3	165·9	71·0
sulphate	$CoSO_4$	155·0	38·0
	$CoSO_4 . 7H_2O$	281·1	21·0
borate	$3CoO . 2B_2O_3 . 4H_2O$	436·6	40·6
oleate	$Co(C_{18}H_{33}O_2)_2$	621·7	9·5
stearate	$Co(C_{18}H_{35}O_2)_2$	625·7	9·4
palmitate	$Co(C_{16}H_{31}O_2)_2$	569·6	10·4
naphthenate			12·0
linoleate			10·0
resinate			8·0
tungate			10·1
COPPER	Cu	63·6	100·0
Copper—			
sulphate	$CuSO_4$	159·6	39·8
	$CuSO_4 . 5H_2O$	249·7	25·5
acetate	$Cu(CH_3 . COO)_2H_2O$	199·7	31·9
chloride	$CuCl_2$	134·5	47·3
	$CuCl_2 . 2H_2O$	170·5	37·3
hydroxide	$Cu(OH)_2$	97·6	65·2
nitrate	$Cu(NO_3)_2 3H_2O$	241·6	26·3
	$Cu(NO_3)_2 . 6H_2O$	295·7	21·5
oxide	CuO	79·6	79·9
Cuprous—			
oxide	Cu_2O	143·1	88·9
sulphate	Cu_2SO_4	223·2	57·0
Copper—			
oleate	$Cu(C_{18}H_{33}O_2)_2$	626·3	10·2
stearate	$Cu(C_{18}H_{35}O_2)_2$	630·3	10·1
palmitate	$Cu(C_{16}H_{31}O_2)_2$	574·2	11·1
linoleate			10·7
naphthenate			12·8
resinate			8·6
tungate			10·8
IRON	Fe	55·8	100·0
Ferric—			
nitrate	$Fe_2(NO_3)_6 12H_2O$	699·9	16·0
	$Fe_2(NO_3)_6 . 18H_2O$	808·0	13·8
chloride	Fe_2Cl_6	324·4	34·4
	$Fe_2Cl_6 . 12H_2O$	540·6	20·7
hydroxide	$Fe_2(OH)_6$	213·7	52·3
oxide	Fe_2O_3	159·7	69·9
sulphate	$Fe_2(SO_4)_3$	399·9	27·9
	$Fe_2(SO_4)_3 9H_2O$	562·0	19·9
ferrocyanide	$Fe_4(FeC_6N_6)_3$	859·2	26·0
acetate	$Fe(CH_3COO)_3$	233·0	24·0

METALLIC CONTENTS OF DRIERS, SALTS AND SOAPS—*Continued*

Drier, Salt or Soap.	Formula.	M.Wt.	% Metal.
Ferrous—			
chloride	$FeCl_2 . 4H_2O$	198·8	28·1
	$FeCl_2$	126·8	44·0
acetate	$Fe(CH_3COO)_2 . 4H_2O$	245·9	22·7
sulphate	$FeSO_4$	151·9	36·8
	$FeSO_4 . 7H_2O$	278·0	20·1
Iron—			
oxide	Fe_3O_4	231·5	72·4
stearate	$Fe(C_{18}H_{35}O_2)_3$	905·9	6·2
oleate	$Fe(C_{18}H_{33}O_2)_3$	899·9	6·2
palmitate	$Fe(C_{16}H_{31}O_2)_3$	821·9	6·8
linoleate			6·6
naphthenate			7·9
resinate			5·2
tungate			6·6
LEAD	Pb	207·2	100·0
Lead—			
acetate	$Pb . (CH_3COO)_2 . 3H_2O$	379·3	54·7
	$Pb . (CH_3COO)_2 10H_2O$	505·4	41·0
borate	$Pb(BO_2)_2H_2O$	311·0	66·5
dioxide	PbO_2	239·2	86·6
oxide	PbO	223·2	92·8
Red lead	Pb_3O_4	685·6	90·7
Lead—			
hydroxide	$Pb(OH)_2$	241·2	85·9
nitrate	$Pb(NO_3)_2$	331·2	62·5
White lead	$2PbCO_3 . Pb(OH)_2$	775·6	80·2
Lead—			
oleate	$Pb(C_{18}H_{33}O_2)_2$	769·7	26·9
stearate	$Pb(C_{18}H_{35}O_2)_2$	773·7	26·8
palmitate	$Pb(C_{16}H_{31}O_2)_2$	717·7	28·9
linoleate			28·2
naphthenate			32·5
resinate			23·4
tungate			28·3
MAGNESIUM	Mg	24·3	100·0
Magnesium—			
carbonate	$MgCO_3$	84·3	28·9
chloride	$MgCl_2$	95·2	25·6
	$MgCl_2 6H_2O$	203·2	12·0
hydroxide	$Mg(OH)_2$	58·3	41·7
nitrate	$Mg(NO_3)_2 6H_2O$	256·4	9·5
oxide	MgO	40·3	60·3
phosphate	$Mg_3(PO_4)_2 4H_2O$	335·1	21·8
sulphate	$MgSO_4 . H_2O$	138·4	17·6
	$MgSO_4 . 7H_2O$	246·5	9·9
	$MgSO_4$	120·4	20·2
acetate	$Mg(CH_3COO)_2 . 4H_2O$	214·4	11·4
oleate	$Mg(C_{18}H_{33}O_2)_2$	587·1	4·2
palmitate	$Mg(C_{16}H_{31}O_2)_2$	535·0	4·6
stearate	$Mg(C_{18}H_{35}O_2)_2$	591·1	4·1
linoleate			4·4
naphthenate			5·3
resinate			3·5
tungate			4·4

METALLIC CONTENTS OF DRIERS, SALTS AND SOAPS—*Continued*

Drier, Salt or Soap.	Formula.	M.Wt.	% Metal.
MANGANESE	Mn	54·9	100·0
Manganese—			
dioxide	MnO_2	86·9	63·2
sesquioxide	Mn_2O_3	157·9	34·9
oxide hydrated	$Mn_2O_3(OH)_2$	175·9	62·5
sulphate	$Mn_2(SO_4)_3$	398·0	27·6
	$MnSO_4$	151·1	36·4
	$MnSO_4 . H_2O$	169·0	32·5
	$MnSO_4 . 4H_2O$	223·0	24·7
	$MnSO_4 . 2H_2O$	187·0	29·4
	$MnSO_4 . 7H_2O$	277·1	19·8
	$MnSO_4 . 3H_2O$	205·0	26·8
	$MnSO_4 . 5H_2O$	241·1	22·8
	$MnSO_4 . 6H_2O$	259·1	21·2
acetate	$Mn(CH_3COO)_2 3H_2O$	227·0	24·2
	$Mn(CH_3COO)_2 4H_2O$	245·0	22·4
borate	$Mn_3(BO_3)_2$	282·8	58·3
carbonate	$MnCO_3$	114·9	47·8
oxalate	$Mn(COO)_2$	142·9	38·5
oleate	$Mn(C_{18}H_{33}O_2)_2$	617·7	8·9
palmitate	$Mn(C_{16}H_{31}O_2)_2$	565·7	9·7
stearate	$Mn(C_{18}H_{35}O_2)_2$	621·7	8·8
linoleate			9·4
naphthenate			11·3
resinate			7·5
tungate			9·5
MERCURY	Hg	200·6	100·0
Mercuric—			
chloride	$HgCl_2$	271·5	73·9
nitrate	$Hg(NO_3)_2$	324·6	61·8
	$Hg(NO_3)_2 . 2H_2O$	360·7	55·6
oxide	HgO	216·6	92·6
sulphate	$HgSO_4$	296·7	67·6
acetate	$Hg(CH_3COO)_2$	318·7	63·0
Mercurous—			
chloride	Hg_2Cl_2	472·1	85·0
nitrate	$Hg_2(NO_3)_2$	525·2	76·3
	$Hg_2(NO_3)_2 . 2H_2O$	561·2	71·5
oxide	Hg_2O	417·2	96·2
sulphate	Hg_2SO_4	497·3	80·7
Mercuric—			
oleate	$Hg(C_{18}H_{33}O_2)_2$	763·3	26·3
palmitate	$Hg(C_{16}H_{31}O_2)_2$	711·3	28·2
stearate	$Hg(C_{18}H_{35}O_2)_2$	767·3	26·2
linoleate			27·5
naphthenate			31·8
resinate			22·8
tungate			27·7
NICKEL	Ni	58·7	100·0
Nickel—			
chloride	$NiCl_2$	129·6	45·3
	$NiCl_2 . 6H_2O$	237·6	24·7
hydroxide (ic)	$Ni_2O_3 . + H_2O$ (indefinite)		55·6
nitrate	$(NiNO_3)_2 6H_2O$	290·8	20·2
hydroxide	$Ni(OH)_2$	92·7	63·3
acetate	$Ni(CH_3COO)_2$	176·7	33·2

METALLIC CONTENTS OF DRIERS, SALTS AND SOAPS—*Continued*

Drier, Salt or Soap.	Formula.	M.Wt.	% Metal.
Nickel—			
acetate	$Ni(CH_3COO)_2 . 4H_2O$	248·7	23·6
formate	$Ni(H . COO)_2 . 2H_2O$	184·7	31·8
oxalate	$Ni(COO)_2 . 2H_2O$	182·7	32·1
oxide	NiO	74·7	78·6
sesquioxide	Ni_2O_3	165·4	35·5
sulphate	$NiSO_4$	154·7	38·0
	$NiSO_4 . 6H_2O$	262·8	22·3
	$NiSO_4 . 7H_2O$	280·9	20·9
oleate	$Ni(C_{18}H_{33}O_2)_2$	621·4	9·5
palmitate	$Ni(C_{16}H_{31}O_2)_2$	569·4	10·3
stearate	$Ni(C_{18}H_{35}O_2)_2$	625·4	9·4
linoleate			10·0
naphthenate			12·0
resinate			8·0
tungate			10·1
Potassium	K	39·1	100·0
Potassium—			
acetate	$K . CH_3COO$	98·1	39·9
bicarbonate	$KHCO_3$	100·1	39·1
carbonate	K_2CO_3	138·2	56·6
	$K_2CO_3 . 2H_2O$	174·2	44·9
chloride	KCl	74·6	52·4
hydroxide	KOH	56·1	69·8
nitrate	KNO_3	101·1	38·7
sulphate	K_2SO_4	174·3	44·9
oleate	$K . C_{18}H_{33}O_2$	320·5	12·2
palmitate	$K . C_{16}H_{31}O_2$	294·4	13·3
stearate	$K . C_{18}H_{35}O_2$	322·5	12·1
linoleate			17·5
naphthenate			20·7
resinate			14·2
tungate			17·6
Sodium	Na	23·0	100·0
Sodium—			
acetate	$Na . CH_3COO$	82·0	28·0
	$Na . CH_3COO . 3H_2O$	136·1	16·9
bicarbonate	$NaHCO_3$	84·0	27·4
carbonate	Na_2CO_3	106·0	43·4
	$Na_2CO_3 . H_2O$	124·0	37·1
	$Na_2CO_3 . 10H_2O$	286·2	16·1
chloride	$NaCl$	58·5	39·4
hydroxide	$NaOH$	40·0	57·5
sulphate	Na_2SO_4	142·1	32·4
	$Na_2SO_4 . 7H_2O$	268·2	17·2
	$Na_2SO_4 . 10H_2O$	322·2	14·3
oleate	$Na . C_{18}H_{33}O_2$	304·4	7·6
palmitate	$Na . C_{16}H_{31}O_2$	278·2	8·3
stearate	$Na . C_{18}H_{35}O_2$	306·4	7·5
linoleate			8·0
naphthenate			9·6
resinate			6·3
tungate			8·1
Thorium	Th	232·4	100·0
Thorium—			
chloride	$ThCl_4$	374·2	62·0

METALLIC CONTENTS OF DRIERS, SALTS AND SOAPS—*Continued*

Drier, Salt or Soap.	Formula.	M.Wt.	% Metal.
Thorium—			
nitrate	$Th(NO_3)_4$	480·4	48·4
	$Th(NO_3)_4 . 4H_2O$	552·2	42·1
	$Th(NO_3)_4 . 12H_2O$	696·6	33·4
sulphate	$Th(SO_4)_2$	424·2	54·8
	$Th(SO_4)_2 . 4H_2O$	496·3	46·8
	$Th(SO_4)_2 . 9H_2O$	586·4	39·7
oxide	ThO_2	264·4	87·9
oleate	$Th(C_{18}H_{33}O_2)_4$	1357·6	17·1
palmitate	$Th(C_{16}H_{31}O_2)_4$	1253·5	18·5
stearate	$Th(C_{18}H_{35}O_2)_4$	1365·5	17·0
linoleate			18·0
naphthenate			21·3
resinate			14·6
tungate			18·1
TITANIUM	Ti	48·1	100·0
Titanium—			
dioxide	TiO_2	80·1	60·1
tetrachloride	$TiCl_4$	189·9	25·2
sulphate	$Ti_2(SO_4)_3$	383·9	25·1
sesquisulphate	$Ti_2(SO_4)_3 . 8H_2O$	528·4	18·2
oleate	$Ti(C_{18}H_{33}O_2)_4$	1173·6	4·1
palmitate	$Ti(C_{16}H_{31}O_2)_4$	1069·5	4·5
stearate	$Ti(C_{18}H_{35}O_2)_4$	1181·6	4·1
linoleate			4·4
naphthenate			5·3
resinate			3·4
tungate			4·4
TIN	Sn	118·7	100·0
Stannic—			
chloride	$SnCl_4$	260·5	45·6
	$SnCl_4 . 3H_2O$	314·6	37·7
	$SnCl_4 . 4H_2O$	332·6	35·7
	$SnCl_4 . 5H_2O$	350·6	33·9
Stannous—			
chloride	$SnCl_2$	189·6	62·6
	$SnCl_2 . 2H_2O$	225·7	52·6
Stannic—			
oxide	SnO_2	150·7	78·8
sulphate	$Sn(SO_4)_2 . 2H_2O$	346·9	34·3
Stannous sulphate	$SnSO_4$	214·7	55·3
Stannic—			
oleate	$Sn(C_{18}H_{33}O_2)_4$	1244·2	9·5
palmitate	$Sn(C_{16}H_{31}O_2)_4$	1140·1	10·4
stearate	$Sn(C_{18}H_{35}O_2)_4$	1252·2	9·5
linoleate			10·1
naphthenate			12·1
resinate			8·0
tungate			10·2
VANADIUM	V	51·0	100·0
Vanadium—			
dichloride	VCl_2	121·9	41·9
trichloride	VCl_3	157·4	32·4
tetrachloride	VCl_4	192·8	26·4
oleate	$V(C_{18}H_{33}O_2)_4$	1176·5	4·3
palmitate	$V(C_{16}H_{31}O_2)_4$	1072·4	4·8

METALLIC CONTENTS OF DRIERS, SALTS AND SOAPS—*Continued*

Drier, Salt or Soap.	Formula.	M.Wt.	% Metal.
Vanadium—			
stearate . .	$V(C_{18}H_{35}O_2)_4$	1184·5	4·3
linoleate . .			4·6
naphthenate . .			5·6
resinate . .			3·6
tungate . .			4·6
ZINC . . .	Zn	65·4	100·0
Zinc—			
acetate . .	$Zn(CH_3COO)_2$	183·4	35·7
	$Zn(CH_3COO)_2 . 2H_2O$	219·4	29·8
nitrate . . .	$Zn(NO_3)_2 . 3H_2O$	243·4	26·9
	$Zn(NO_3)_2 . 6H_2O$	297·5	22·0
oxide . . .	ZnO	81·4	80·4
sulphate . .	$ZnSO_4$	161·4	40·5
	$ZnSO_4 . 6H_2O$	269·5	24·3
	$ZnSO_4 . 7H_2O$	287·5	22·7
chloride . .	$ZnCl_2$	136·3	48·0
oleate . . .	$Zn(C_{18}H_{33}O_2)_2$	628·1	10·4
palmitate . .	$Zn(C_{16}H_{31}O_2)_2$	576·1	11·4
stearate . .	$Zn(C_{18}H_{35}O_2)_2$	632·1	10·4
linoleate . .			11·0
naphthenate . .			13·2
resinate . .			8·8
tungate . .			11·1
ZIRCONIUM . .	Zr	91·2	100·0
Zirconium—			
chloride . .	$ZrCl_4$	232·4	39·3
oxide . . .	ZrO_2	122·6	74·4
sulphate . .	$Zr(SO_4)_2 . 4H_2O$	355·4	25·7
oleate . . .	$Zr(C_{18}H_{33}O_2)_4$	1216·7	7·5
palmitate . .	$Zr(C_{16}H_{31}O_2)_4$	1112·6	8·2
stearate . .	$Zr(C_{18}H_{35}O_2)_4$	1224·7	7·5
linoleate . .			8·0
naphthenate . .			9·6
resinate . .			6·3
tungate . .			8·0

CHAPTER 11

ANTIOXIDANTS

ANTIOXIDANTS are known also as inhibitors or negative catalysts.

Antioxidants are agents which retard the normal oxidation process of drying compositions. Their presence may be inconvenient, and it is then necessary to effect their removal. Thus, unprocessed drying oils contain natural antioxidants which cause the so-called induction period. Although a drying composition is exposed to oxidising conditions, no perceptible oxidation may occur for some time. This time of apparent inactivity is known as the induction period.

Alternatively, antioxidants may be added to varnishes to control excessive oxidation, which is reflected in rivelling, skinning or diminished durability. Thus antioxidants may be either a disadvantage or, if used with care, of great value.

Natural Antioxidants.—Hamilton and Olcott [1] have stated that the induction period of natural drying oils is due to the presence of inhibitors or antioxidants, pure materials having no induction period. This contention is supported by the results of experiments conducted on the oxidation of methyl oleate. Cohen includes among the probable natural antioxidants of linseed oil, chlorophyll, xanthophyll, carotene, and the phosphatide, cephalin. Cephalin has been detected in the aqueous extraction of linseed oil.[2]

It is interesting to note, however, that under certain conditions carotene may effectively reduce the induction period.[3] Taufel and Müller have shown also that chlorophyll and xanthophyll can increase the rate of drying of oils. The rate of drying and autoxidation of pumpkin seed oil were reduced by treatment with Fuller's earth. The subsequent addition of chlorophyll partly restored these properties.[42]

It seems probable that what is commonly known as the "break" of oils is closely related to the natural antioxidants, for Kraybill, Kleinsmith, and Thornton have shown that the drying times of soya bean oils vary with the "break" and phosphatide content, and that when these and other substances are removed, drying times become uniform.[4] Hilditch and Paul believe that a basic oxygen compound is the antioxidant in natural seeds.[5] Antioxidants resembling vitamin E have been isolated by Olcott and Mattill from the unsaponifiable matter of vegetable oils.[6] Soya bean meal is digested with an organic acid and then extracted with methyl alcohol. When this extract is further extracted with cold acetone a resinous material is obtained which is a strong antioxidant.[7]

The composition of the phosphatides of three vegetable oil seeds are given in the table [43] on the following page.

Vegetable Oil Seed	Lecithin, Per cent	Cephalin, Per cent
Cottonseed . .	28·8	71·2
Linseed . .	36·2	63·8
Sunflower . .	38·5	61·5

Removal and Destruction of Antioxidants.—It is claimed that the natural antioxidants of linseed and olive oils may be destroyed by boiling water or removed by extraction with water. The effect produced in olive oil by antioxidant is said to be equal to that produced by 0·03 per cent of quinol.[8]

A method has been recorded whereby the induction period of soya bean oil can be reduced from 200 to 20 hours.[9] According to Cohen, the induction period of linseed oil is curtailed by adding manganese driers, by ageing, and by heating (200°–270° C.). The explanation offered for the effectiveness of these methods is that the phosphatides and carotenoids are readily oxidised.[10]

The addition of lead linoleate, resinate or naphthenate to raw oil seems to cause precipitation of the natural antioxidants.[11]

The Mechanism of Oxidation Inhibition.—The extent to which dry is inhibited by antioxidants depends upon the amount of antioxidant present. In some cases, however, small amounts of antioxidants may act as pro oxidants, and it is only with larger amounts that they exert their normal retarding influence.[12]

The mechanism of the process by which antioxidants cause inhibition of drying is not clear. Scheiber suggests that the antioxidant reduces the peroxides of the oil in two stages :

$$AO_2 + X = AO + XO$$
$$AO + XO = A + X + O_2$$

where the antioxidant is represented by X.[13] Some antioxidants react with oxygen themselves, a reaction stimulated by the presence of drying oils. Quinol appears to be unique in its action, for there is evidence that it forms an unstable additive compound with unsaturated acids.[14]

The oxidation process following the induction period is said to be unaffected by the presence of phenolic antioxidants.[1] Lederer agrees that the course of the oxidation process is unaffected, and that what occurs is merely a diminution in the rate of oxygen absorption.[15]

Artificial Antioxidants.—Resorcinol and β-naphthol delay the setting of tung oil, but do not substantially affect the amount of oxygen absorbed during drying. With linseed oil the activity of these antioxidants is said to be gradually destroyed. The inhibition of autoxidation by means of antioxidants is said to be more marked with dehydrated castor oils than with linseed or tung oils.[16] Guaiacol, maleic acid, and mannitol increase the induction period when lard and cod liver oil are oxidised at 50° C.[3]

Benzoin resin, Tolu balsam and various phenols are also given as effective antioxidants for lard.

Antioxidants for edible oils include lecithin,[17] quinol, diphenyl guanidine and potassium cyanide. 0·1 per cent of benzyl alcohol, phenyl ethyl alcohol or cinnamyl alcohol is a satisfactory antioxidant for castor or arachis oils.[18] The rate of oxygen absorption of linseed oil is reduced by 50 per cent by the addition of a trace of acetoxime.[19]

Some phenolic resins in conjunction with linseed oil act as antioxidants, and this may be due to free phenols in the resin. Vernon and Rinne have studied this aspect, and have shown that sometimes the antioxidant effect can be reduced by treatment with hydrogen peroxide.[20]

Other antioxidants which are effective for drying oils are guaiacol, pyrocatechol, eugenol, the monomethyl ether of hydroquinone,[21] and pyrogallol. Anilido-ethane thiol has been suggested as a satisfactory antioxidant for many substances which normally oxidise readily.[22] Hilpert and Niehaus record the results of inconclusive experiments on the antioxidant effect of phenols on linseed and tung oils in the presence of lead, cobalt and manganese driers.[23]

Morvillez, Balâtre and Pujo state that the tendency of a substance to reduce ammoniacal silver nitrate is an indication of antioxidant activity.[24]

Uses

The oxidation inhibiting properties of the antioxidants have been exploited in many directions, although such additions are by no means popular yet. In adding antioxidants to drying compositions, the greatest difficulty is to accomplish the desired result without introducing other defects. Two defects which are introduced are retardation of drying, and the acquisition of a smell which is not always pleasant. On ageing the smell disappears, and it is usually only during the very early life of the film that it is unmistakably present. In this connection, it is interesting to note the observations of Hilpert and Niehaus, who have recorded that during the drying of oils phenols seem to disappear. Their disappearance is not due to evaporation, but is a gradual process involving three stages.[25]

Failure of air-drying compositions on exposure is usually attributed, at least in part, to the disintegrating action of continued oxidation. It is not surprising, therefore, that antioxidants have been used to control this gradual oxidation. The durability of phenolic resin-tung oil varnishes has been improved by the addition of 0·72 per cent (calculated on non-volatile portion) of various antioxidants.[26] Aryl substituted guanidine has been used to help maintain flexibility in air-drying compositions without adversely affecting the dry.[27]

One of the most well-known uses for antioxidants is to prevent the skinning of varnishes or pigmented compositions in the containers during storage. When used for this purpose they are known as anti-skinning agents. The problem of skinning may be tackled in four ways.

1. The product may be reformulated to eliminate or to partly eliminate

raw materials which cause skinning. Alternatively, the varnish may be subjected to a modified heat treatment with advantage.

2. The varnish, etc., may be stored in absence of air. This is accomplished by almost completely filling the containers or by replacing air with an inert gas like carbon dioxide.

3. Antioxidants may be added.

4. Dispersing agents may be incorporated.

Many antioxidants, including proprietary articles, have been suggested to minimise skinning. The object is to add sufficient antioxidant to prevent skinning, but insufficient to seriously impede the drying of the film. This is a very difficult accomplishment and most adjustments, therefore, are compromises. Among anti-skinning agents may be included, beechwood creosote, guaiacol, cresol, *o*-amyl phenol, pyrocatechol, pyrogallol, hydroquinone, eucalyptus oil, clove oil, Guaiaphene, and Albertol 109J.[28] *o*-Amyl phenol is obtained as a by-product during the manufacture of *p*-tertiary amyl phenol. It is obvious that polyhydroxyphenols or their derivatives are satisfactory anti-skinning agents. Pyrocatechol appears to be the most powerful anti-skinning agent readily available. Guaiacol is satisfactory also, but is not so effective as pyrocatechol. Guaiaphene is a proprietary article derived from pine wood, containing a mixture of phenols among which are pyrocatechol, pyrogallol, guaiacol and their derivatives.[29] Albertol 109J is used at 3–6 per cent in varnishes.[30] The polymerisable bodies of crude solvent naphtha are reacted with phenolic compounds to yield a " phenolic heavy oil " which has anti-skinning properties.[31] An inexpensive anti-skinning agent is made by the condensation of phenols with cyclic compounds possessing a cyclopentadiene nucleus.[32] Compounds containing the oximido group have been patented as anti-skinning agents and are used in amount up to 0·2 per cent of the drying oil present.[40]

Dispersing agents which are used to prevent skinning may be either acidic compounds or solvents. Among the acidic compounds are α-crotonic acid, sold under the designation of Mittel 29, salicylic acid and benzoic acid. Solvent dispersing agents are: cyclohexanol, methyl cyclohexanol, dipentene, pine oil, butyl alcohol and butyl glycollate. Dipentene is stated to reduce surface tension.[29]

Frequently, combinations of anti-skinning agents are used. Such combinations utilise the properties of the phenolic compounds and the solvents.

Another use of antioxidants is in the control or elimination of excessive surface oxidation which manifests itself as rivelling. Carboxylic acids with triple bonds or their derivatives have been patented for this purpose, and the following represents a list of suitable compounds:

$$CH_3C{\equiv}C.COOH,\ CH{\equiv}C.COOH,\ ClC{\equiv}C.COOH,\ OIC_6H_4C{\equiv}C.CCOH,\ NO_2C_6H_4C{\equiv}C.COOH \text{ and } C_6H_5{\equiv}C.COOH.$$ [33]

Although metallic soaps like those of zinc and copper are not normally

regarded as antioxidants, they may claim this description when they are used to prevent rivelling.

Other uses of antioxidants are to prevent thickening of enamels and to control the rate of viscosity increase of oils.[12] The rate of viscosity increase during the blowing of rape oil is reduced by the presence of cobalt linoleate (0·1 per cent cobalt), quinol (0·25 per cent), phenylhydrazint (0·1 per cent.) and anthranilic acid (1 per cent).[34] Antioxidants also prevent the polymerisation of peroxides.[35] The effect of soluble cobalt soaps on the viscosity of rubber solution is well known, but it can be inhibited by antioxidants, examples of which are α and β-naphthols, pyrogallol, oxyhydroquinone, *o* and *p*-aminophenols and amines such as *di*-phenylamine, and α and β-naphthylamines.[36]

The discoloration of heavy metal naphthenates and resinates on oxidation, is eliminated by adding antioxidants, among which are *p*-phenylene diamine, *o* and *p*-aminophenols, and fractions with a boiling-point in excess of 240° C. obtained from wood tar. Combinations of these compounds yield very satisfactory results, and a mixture of methylated *p*-aminophenol (4 pts.) and methylated *p*-phenylenediamine (1 pt.) is suggested.[37]

Certain drying oils under favourable conditions may ignite spontaneously, especially in the form of thin films. Blitz and Simon have conducted experiments with anti-oxidants to inhibit or retard the spontaneous ignition of oils. Three phenolic compounds were tested separately with linseed, sunflower and tung oils. The ignition of tung oil could not be retarded satisfactorily by any of the phenols—pyrocatechol, α- or β-naphthol. The greatest retardation was given by pyrocatechol and the least by β-naphthol.[41]

Work has been conducted on the prevention of the deterioration of cracked gasolines by antioxidants.[38]

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CHAPTER 12

ASPHALTUMS AND PITCHES

Nomenclature.—The nomenclature of these materials is by no means clearly understood in the varnish trade. The terms, asphalt, asphaltum, pitch and bitumen are used indiscriminately with practically no pretence at accuracy. Thus any black resinous substance is described as a bitumen or a pitch, whether it is Gilsonite, Rafaelite, Manjak, an asphaltic petroleum product, or substances obtained by distillation of rosin, wool grease, or vegetable oils. A material with similar characteristics to Gilsonite is erroneously described as Density pitch. Since it is obviously a natural asphaltum, a better description would be Density asphaltum.

According to Peckham [1] "bitumen is a generic term used to designate a class of minerals, as they occur in nature, that are soluble in chloroform and other neutral liquids." "Artificial bitumen" is a name applied to distillation residues such as those from coal tar, petroleum, etc. Langton [2] also regards the term "bitumen" as a generic one, describing substances soluble in carbon disulphide, or other neutral liquids, of which carbon and hydrogen are the major constituent elements. The term "bitumen" may be amplified to describe more precisely a certain type of substance, e.g. "artificial" or "mineral" bitumens. The B.S.I. definition of "bitumen" is "a generic term for a group of hydrocarbon products soluble in carbon disulphide, which either occur in nature or are obtained by the evaporation of asphaltic oils. The term shall not include residues from paraffin oils or coal-tar products."

Asphalt or asphaltum describe the hard natural bitumens, such as Gilsonite, Rafaelite, Manjak, etc., but the latter term is preferable to the former because asphalt is often applied specifically to bitumens containing mineral matter. This may be present in the bitumen naturally or it may have been added deliberately. In any case those materials are not used in the varnish trade. The softer bitumens are known as Malthas. Natural asphaltums of the Gilsonite or Manjak varieties are also known as asphaltites.

The term "pitch" or "residual pitch" describes the distillation residues obtained from coal tar, rosin, or petroleum, etc.

Source.—The U.S.A. is a prolific producer of bituminous materials, which occur in Connecticut, New York State, New Jersey, Virginia, Texas, Colorado, Utah, Kentucky, California and Oklahoma. Other sources are Barbadoes, Trinidad, Venezuela, Cuba, Mexico, Egypt, Persia, Albania, Sicily, Argentine, Hanover, the Rhone Valley and the shores of the Dead Sea.

Composition.—Asphaltums are mixtures of complex compounds built up from the elements, carbon, hydrogen, oxygen, sulphur and nitrogen,

of which the two former predominate. They may contain, in addition, organic salts of iron and aluminium, silica and free carbon. It will be readily appreciated that the chemical constitution of the compounds present in residual pitches obtained from vegetable oils, coal tar, rosin, or wool grease, will differ greatly from those either in the asphaltums or in the asphaltic products originating in petroleum.

Properties

The order of importance to the varnish maker of bituminous and similar materials is, firstly, Gilsonite and natural asphaltums with similar properties, then asphaltic bitumens from petroleum, Manjak, coal-tar pitch, and stearine pitch. Other types are used only rarely. Due to difficulties consequent upon the recent war, and subsequently, supplies of American asphaltums have sometimes been restricted. The better availability if Rafaelite has attracted interest in this asphaltum, which is new to the trade, and it is predicted that it will permanently replace Gilsonite for certain purposes. It is not too imaginative to visualise Rafaelite holding pride of place with Gilsonite ultimately, if certain difficulties of manipulation can be overcome.

Gilsonite.—Gilsonite is a natural asphaltum obtained from Utah. Wurtzilite and Nigrite occur in the same vicinity. An asphaltum similar to Gilsonite comes from Texas and Colorado. Gilsonite is a brittle substance exhibiting a conchoidal fracture. It is a good black with a brilliant lustre. It is readily soluble in petroleum hydrocarbons, including benzine, white spirit, distillate and paraffin ; in aromatic hydrocarbons, coal-tar naphthas, turpentine and similar terpene solvents, chlorinated hydrocarbons, carbon disulphide, and treated and untreated vegetable oils. Compatibility with other varnish raw materials is generally good. Gilsonite is insoluble in alcohol, and only partly soluble in low boiling petroleum ethers.

The properties of Gilsonite and other asphaltums can be modified by special heat treatment. A patented process involves sweating the asphaltum at abnormal temperatures (370°–400° C.) for three to ten hours. This results in the production of a residue with a reduced melting-point useful for the manufacture of black varnishes.[3] Heat treatment of Gilsonite over the same temperature range is said to increase the fixed carbon content from 20–65 per cent.[4]

Grahamite.—This asphaltum occurs in Oklahoma and Virginia. It is similar to Gilsonite, but harder. When fractured, the surface may be bright or dull, according to the position of the specimen in the seam. Density asphaltum is also similar to Gilsonite, except that it is harder and more opaque. The author has been unable to establish if any relationship exists between Grahamite and Density asphaltum. The latter-named product is used in fair quantities in this country for the same purposes as Gilsonite, for its solubility in varnish components is identical.

Rafaelite.—Rafaelite is mined in the Argentine. It is distinguished from Gilsonite by reason of its greater hardness, higher melting-point, colour of streak on porcelain, better opacity and lesser compatibility. It breaks with a conchoidal fracture and the exposed surfaces have excellent lustre. Rafaelite is soluble in aromatic and chlorinated hydrocarbons and carbon disulphide. It is less soluble in turpentine, and even less soluble still in white spirit as evidenced by the high viscosities of the resultant solutions. Compatibility with drying oils within limits is satisfactory, when care is taken in incorporation, but this aspect is elaborated later. Like Gilsonite, Rafaelite is almost completely insoluble in ethyl alcohol.

It contains practically no volatile matter, even at high temperatures. Six hours at 525° F. produce only a small fractional percentage loss. At 25° C. penetration is nil. The sulphur content is approximately 2¼ per cent.

Its excellent opacity or staining power enables it to be diluted with cheaper bituminous materials, such as stearine pitch or blown products, or with resins and oils. The exploitation of the introduction of resin or oil is a valuable weapon to the formulator, for it assists him to overcome certain film defects common to finishes based on asphaltums and pitches.

The water absorption of Rafaelite is claimed to be lower than that of other natural asphaltums. Compared with finishes based on Gilsonite, those on Rafaelite have similar durability under normal conditions of exposure, although there are indications that Gilsonite gives slightly better durability under accelerated weathering. Generally, Gilsonite films have superior gloss.

Asphaltic Bitumens from Petroleum.—Petroleum bitumens are obtained from the asphaltic type of crude petroleum containing cyclic hydrocarbons, and occur as the distillation residue. Distillation may be conducted in the presence of steam. Black bitumens with low softening points are obtained by cracking fuel oil residues. In contradistinction to the asphaltic crudes there are the so-called paraffinic crudes. The final products from the distillation of paraffinic crudes are lubricating oils and waxes, not asphalts. There is a similarity of properties between natural asphaltums and the asphaltic bitumens from petroleum. This has been explained by the fact that the natural asphaltums are also residues, probably derived from the evaporation of petroleum.

Petroleum bitumens are widely used in varnish manufacture. They possess the advantage that unlike the natural asphaltums they are available in a carefully graduated scale of physical properties. The following tables are illustrative of this. They vary from soft sticky pastes, almost pourable, to products with melting-points of 120° C. or higher. Products with melting-points up to 210° C. are obtainable. Both melting-point and hardness increase with the asphaltene content. Compatibility with the common varnish solvents, oils and resins, is excellent, and no special treatment is necessary for blending.

Asphaltic petroleum bitumens are characterised by low ash content by comparison with the natural asphaltums.

Blown asphaltic Bitumens.—These are not much used by the varnish maker except for special purposes. They are the residues obtained by dehydrogenation and polymerisation of petroleum. This is accomplished by passing air and steam through at elevated temperatures. They are more rubbery, and have less gloss than the unblown products. Their compatibility with other varnish ingredients is much inferior, and this is especially noticeable in straight solutions in the common varnish thinners. Where they are soluble, excessive amounts of thinners are necessary to obtain a solution of workable viscosity. Solubility difficulties have prevented the growth of popularity of blown bitumens in spite of their useful flexibility.

They have good chemical resistance, and solutions of selected blown bitumens in chlorinated hydrocarbons have found application in the coating of vats subject to chemical attack.

Colourless, Albino, Light, or Pale Petroleum Bitumens, or Light Petroleum Resins.—The term "colourless" is misleading, for the best of these materials are a deep golden-yellow colour. Most bitumens, natural or artificial, and pitches, are much too intensely black to permit their use in media for pigmentation with pigments of delicate shades. Adsorption of asphaltenes on agglomerates of carbonaceous matter is said to be the cause of the intense colour. Whilst the problem of producing enamels or paints in pale tints, based on bituminous products, has not been solved satisfactorily, it is possible by the use of pale bitumens to obtain enamels in colours other than black. Light browns, reds, greens, and dark blues can be made with ease. Since bituminous paints are used for specific purposes, such as for chemical and heat resistance, the pigments most commonly used are umber, sienna, red and yellow iron oxides, chromium oxide and titanium oxide.

Light asphaltic bitumens or petroleum resins can be produced by several different methods. The first consists in selecting a certain type of crude petroleum and subjecting it to very careful distillation. Pale bitumens contain the minimum amount of asphaltenes. An alternative method is the removal of colour from a bitumen by a more costly chemical treatment. Sulphuric acid or bleaching earths such as fuller's earth are used for this purpose. Another more modern method involves the propane extraction of selected lubricating oil fractions.

Asphaltic light bitumens are soluble in petroleum or aromatic hydrocarbons and are miscible with vegetable oils and natural resins.

Manjak.—Manjak, munjack, or glance pitch is mined in Barbadoes. This type is the one most commonly used in the manufacture of black varnishes. Another grade of higher melting-point occurs in Trinidad.

Manjak is an intense black asphaltum with good staining power. It is extremely difficult to dissolve in hot vegetable oils, and although after heat treatment a substantial percentage remains undissolved, satisfactory

PROPERTIES OF ASPHALTIC BITUMENS FROM PETROLEUM. (I)

	Spramex 400–500.	Spramex 280–320.	Spramex 220–250.	Spramex 200–220.	Mexphalte 90–110.	Mexphalte 60–70.	Mexphalte 40–50.	Mexphalte 30–40.	Mexphalte 20–30.	Mexphalte 10–20.
Specific gravity at 25°–25° C.	1·005	1·009	1·011	1·012	1·017	1·02	1·026	1·033	1·035	1·037
Melting-point (R. and B.) °C.	28–33	31–37	33–39	35–41	43–50	47–55	52–60	54–62	59–66	63–73
Melting-point (R. and B.) °F.	82–91	88–99	91–102	95–106	109–122	117–131	126–140	129–144	138–151	145–163
Ductility at 25° C.		105 min.	105 min.	105 min.	105 min.	105 min.	105 min.	105 min.	30 min.	5 min.
Penetration at 25° C.	400–500	280–320	220–250	200–220	90–110	60–70	40–50	30–40	20–30	10–20
Flash-point (open) °F.	465	510	515	525	550	570	585	600	610	625
Solubility in carbon disulphide: % wt.	99·9	99·9	99·9	99·9	99·9	99·9	99·9	99·8	99·8	99·8
Solubility in carbon tetrachloride: % wt.	99·8	99·8	99·8	99·8	99·8	99·8	99·8	99·7	99·7	99·7
Asphaltenes: % wt.	12	12	12·5	13	14	15	16	17	19	20

(By courtesy of SHELL-MEX AND B.P. LTD.)

PROPERTIES OF HARD AND BLOWN ASPHALTIC BITUMENS FROM PETROLEUM. (II)

				Oxidised or Blown Grades.				
	Mexphalte H. 80–90.	Mexphalte H. 105–115.	Mexphalte H. 110–120.	Mexphalte R. 135–10.	Mexphalte R. 115–15.	Mexphalte R. 85–40.	Mexphalte R. 85–25.	Mexphalte R. 75–30.
Specific gravity at 25°–25° C.	1·05	1·06	1·10	1·048	1·049	1·025	1·047	1·037
Melting-point (R. and B.) °C.	80–90	105–115	110–120	130–140	110–120	80–90	80–90	70–80
Melting-point (R. and B.) °F.	176–194	221–239	230–248	266–284	230–248	176–194	176–194	158–176
Ductility at 25° C.	0–6	0–1	Nil	1 min.	2 min.	3 min.	3 min.	4 min.
Penetration at 25° C.	5–15	3–8	3–7	7–12	10–20	35–45	20–30	25–35
Flash-point (open) °F.	690	675	565	520	465	450	510	500
Solubility in carbon disulphide: % wt.	99·9	99·9	98·0	99·8	99·6	99·9	99·8	99·8
Solubility in carbon tetrachloride: % wt.	99·8	99·8	97·5	97·7	99·5	99·7	99·7	99·7
Asphaltenes: % wt.	25·5	34	40	40	38·5	32	31	32

(By courtesy of SHELL-MEX AND B.P. LTD.)

opacity is given by the soluble portion. Straight solutions of Manjak in white spirit are not practical. In fact, even after incorporation of the Manjak in oil, it is sometimes necessary to bolster up the white spirit thinner with aromatic hydrocarbons to obtain stability. Aromatic or chlorinated hydrocarbons have much better solvent power for this asphaltum than that possessed by white spirit.

PROPERTIES OF LIGHT PETROLEUM RESINS. (III)

Description.	Penetration Value (25° C.).	Melting Pt. (°C.) (R. and B.).
Petroleum resin S. 1 (soft grade)	140–160	39
Petroleum resin H. 1 (hard grade)	14–16	53
Petroleum resin S. 2 (soft grade)	130	39
Petroleum resin H. 2 (hard grade)	17	54
Petroleum resin S. 3 (soft grade)	80–100	44
Petroleum resin H. 3 (hard grade)	20–30	54
Petroleum resin VS. 3 (very soft grade)	180–200	40

(By courtesy of TECHNICAL PRODUCTS LTD.)

Coal-tar Pitch.—Coal-tar pitch is the distillation residue from coal-tar. As with other products obtained by distillation, the resultant pitch from coal tar varies in properties, according to the efficacy and duration of the distillation process. Pitches from different types of coal also vary appreciably. The yield of pitch from coal tar is proportional to the amount of aromatic bodies present. Tars containing large amounts of paraffinic bodies yield less pitch than those rich in aromatics.

Pitches vary in hardness from a soft solid, plastic at ordinary temperature, to a hard brittle product.

They have good staining power, which may be attributed in part, at least, to the free carbon they contain. They are easily recognisable by their characteristic smell.

Unless the harder types of pitch are used, there is a marked tendency for the ultimate films to exhibit appreciable tackiness—a condition which is very inconvenient for normal production methods. The harder pitches dissolved in coal-tar naphthas dry rapidly in about one hour fit to handle, and quite hard in about three or four hours.

Coal-tar pitches are incompatible with most common varnish thinners, as well as with vegetable oils and resins. Consequently they are rarely encountered in varnish compositions containing other ingredients. The varnish maker uses them alone as received from the gas works, except, perhaps, he may purchase the hard pitch and dissolve it, or he may make slight adjustments to the viscosity of the black varnish as received. Coal-tar pitch cannot be thinned with petroleum hydrocarbons, turpentine or alcohol. Aromatic hydrocarbons are necessary and coal-tar naphtha is commonly used. A black varnish or medium suitable for pigmentation consists of a solution of coal-tar pitch in benzene to which crude phenol

is added. Whenever coal tar or solutions of coal-tar pitch are to be used for pigmentation, Stock recommends that they are de-acidified and de-hydrated.[6]

The following pitches may be grouped with coal-tar pitch : water gas, coke oven, blast furnace and lignite tar pitches. Walther has compared coal-tar pitch with high vacuum and air blown bitumens. Coal-tar pitch is more susceptible to temperature changes and mechanical shock than the other two, but it has better adhesion to iron. Coal-tar pitch shows less tendency to form acid oxidation products on exposure, and hence corrodes metal less.[7]

Stearine Pitches.—These pitches vary in properties depending upon the composition of the parent bodies. They are the residues from the distillation by superheated steam of fats, vegetable oils or fatty acids. They are soft ductile pitches with melting-points not exceeding about 90° C. Their primary use, because of their ductility, is to confer elasticity or flexibility on the harder types of asphaltum. Since they are susceptible to atmospheric oxidation, they tend to lose their tackiness and harden on exposure. Opacity is usually of a very low order. Stearine pitches are characterised by their comparatively high saponification and acid values. The solubility of pitches from different sources is variable. Some varieties dissolve readily in petroleum hydrocarbons. Others are much less soluble.

Other Asphaltums and Pitches.—Many other bitumens and pitches exist. They have found, however, as yet, but little application in the manufacture of film-forming compositions. In a generation where progress is rapid, the inclusions of these other types may not be amiss, for they may possess just those peculiar properties essential for the elucidation of a particular formulation problem.

Impsonite.—This is a very hard infusible natural asphaltum occurring in Oklahoma. It is sometimes used to increase the melting-point and opacity of other asphaltums such as Gilsonite. The main reason for its lack of popularity is its incompatibility. It is insoluble in petroleum hydrocarbons and almost insoluble in carbon disulphide. It is incompatible with vegetable oils.

Syrian Asphaltum.—In the United States of America it is known also as Egyptian asphaltum.

It is obtained from mines near Damascus, and is a hard black asphaltum fracturing with a glossy surface. Although it is recorded that this asphaltum is used in durable black japans, only very small quantities in aggregate are involved. Solubility in aromatic hydrocarbons like benzene is good, but it is only slightly soluble in petroleum hydrocarbons. In fact, addition of petroleum hydrocarbon to a benzene solution causes precipitation.

Elaterite.—Elaterite is described by Morrell as a "pyrobituminous asphaltite." It sometimes passes under the name "Mineral Caoutchouc." A sample examined by the Author was a black rubbery solid. On heating,

it demonstrated a tendency to char rather than to melt normally, and consequently solutions in solvents are made by cold churning. Elaterite is soluble in aromatic hydrocarbons such as xylol or naphtha, in chlorinated hydrocarbons, and in turpentine. It is only partly soluble in petroleum hydrocarbons. The films obtained after evaporation of the solvent have poor gloss by comparison with natural asphaltums like Gilsonite, and covering power is much inferior. Elaterite films have little toughness and are easily marked. This defect may be overcome, in part, by admixture with other natural and artificial bitumens, which also effects an improvement in gloss. Resistance to heat of elaterite is superior to that of other asphaltums. Durability on ironwork is inferior to that of both coal-tar pitches and artificial petroleum bitumens.

Sadki Asphaltum.—Work has been conducted on this material by Zhebrovskii and Yudin, and their results indicate that special treatment is necessary in order to make satisfactory varnishes. Thus, extraction of the crude asphaltite with benzene yields an extract which is compatible with oil and is fusible. It gives results similar to those from Gilsonite. Alternatively, the crude asphaltite can be fused with rosin and coumarone resins, and thus rendered soluble in linseed oil.[8]

Bone Pitch.—When bones are subjected to dry distillation a distillate is obtained known as Dippel's oil. The residue obtained on the subsequent distillation of this oil is bone pitch. Bone pitch is a hard lustrous substance of good black colour and outstanding opacity. It is not used to any large extent because of its general incompatibility with varnish constituents. Whenever it is used, it is in conjunction with rosin which acts as a solubilising agent, or with more compatible asphaltums or pitches. It is incompletely soluble either in petroleum or aromatic hydrocarbons.

Wood-tar Pitches.—These are known also as Stockholm, Swedish, Pine or Archangel pitches. They are the residues from the distillation of wood tar. Generally, they have little opacity, being brownish rather than black in colour. They contain both acidic and phenolic bodies and are attacked by alkalies. Durability is poor.

Rosin Pitch.—This pitch is the residue derived from the distillation of rosin. It is a hard brownish material which crumbles easily. Its durability is poor, and it is rarely used in varnish compositions.

Dark Resins.—Certain dark resins are available, and although not possessing the opacity or blackness of the asphaltums or artificial bitumens, they are sometimes used in place of these materials. Very dark grades of coumarone or phenol formaldehyde resin are made, and their depth of colour is utilised. Oxidised rosin is a dark reddish-brown substance, and being soluble in industrial alcohol, provides the basis for some dark spirit stains.

Modifications.—Modifications of natural and artificial bitumens are made. Such modifications include the introduction of steam into the distillation process, oxidation of the non-volatile residues by passing air or oxygen through the molten mass, the conjoint treatment with steam

and air, the sweating of the bitumen at high temperatures, the addition of basic inorganic substances to reduce acidity, and the addition of many other substances. Of the other substances used, sulphur, compounds of sulphur including polysulphides, organic and inorganic peroxides, and per acid salts have been suggested.[9] These substances are incorporated at elevated temperatures, at ordinary, increased, or reduced pressure.

Examination, Testing and Analysis

When used in varnishes or allied compositions, asphaltums and pitches must be tested very carefully. Considerable variation in properties is observed in bituminous products from different sources.

Fracture.—Much information is given by a preliminary visual observation of the materials. Manjak, for example, can be readily differentiated from Gilsonite, Density asphaltum, or even the hard artificial bitumens from petroleum sources, by the dullness of the surface yielded on fracture. The surface has a crystalline appearance. The Gilsonite types or hard petroleum bitumens yield glossy surfaces on fracture.

Manjak differs from these other types also in that it fractures much more easily, and consequently consists chiefly of relatively small lumps and powder. Consignments of Gilsonite and Density asphaltum generally contain large pieces with practically no dust.

Impurities.—A visual observation of Manjak frequently reveals the presence of extraneous insoluble mineral matter. Its different colour makes it readily detected. The care with which the asphaltum is mined influences greatly the amount of impurities present.

Smell.—Asphaltums or pitches from different sources have characteristic smells. The best way to test the smell is to break a piece of the material and smell the freshly exposed surfaces. Rafaelite asphaltum has an appreciable smell resembling that of organic sulphur compounds, but Gilsonite and Density asphaltums have only very weak smells. The smells of bone pitch and coal-tar pitch are also distinctive. If the smell obtained by the above method is too weak, it may be accentuated by gentle warming.

Condition.—A clue to the hardness of a bitumen is given by noting its physical condition. If it retains the form of sharp-edged individual lumps it is a hard bitumen of high melting-point. If the lumps have lost their sharp edges and have tended to coalesce, they are softer with correspondingly lower melting-points. The very soft grades will not comprise lumps, but will have subsided into the shape of the storage container.

Streak on Porcelain.—When bitumens are drawn across a rough porcelain surface they yield streaks varying in colour from light brown to black. Black streaks are given by Manjak, Grahamite, Impsonite, Rafaelite, coal-tar, and wool grease pitches. Brown streaks are given by Gilsonite and pitches derived from whale oil, cottonseed oil, tallow and lard. Bermudez asphaltum and palm oil pitch gives streaks of intermediate colour.

Heat Test.—A simple test which enables Gilsonite to be distinguished from similar but harder grades of asphaltum consists in suddenly applying heat to a small specimen by introducing it into a bunsen flame. Gilsonite melts gently but the harder grades fracture and splinter before fusing.

Solubility

In Thinners.—From the point of view of the varnish maker the solubility of bituminous materials is of primary importance. Of all the solvents with which these materials will be used, a solubility test based on white spirit is the most searching.

The material under examination is fused by heating, and then thinned with a definite amount of white spirit. Since considerable difficulty may be experienced in thinning asphaltums with high melting-points, due to chilling, solution may be effected by cold churning or by refluxing. In comparing asphaltums the harder grades yield solutions of higher viscosity than the softer grades, for the same amounts of thinner. Very hard grades with indifferent solubility in white spirit often give solutions which, on cooling, set to firm gels even with increased amounts of thinners. Asphaltums which require excessive amounts of thinners to obtain solutions of normal working viscosity may be rejected as unsatisfactory because of reduced film thickness. The tendency of an asphaltum solution to gel on cooling is not always immediately apparent. Frequently, gelation requires several days. Hence premature decisions may be erroneous. Solution of most types of asphaltum and pitch in petroleum hydrocarbons, show at least some tendency to stouten on ageing. Providing this is not excessive it may be disregarded, and this particular defect is generally accepted as unavoidable. Such stoutening necessitates the readjustment of viscosity of solutions before they are sent to the customer, if they have been in storage more than a few weeks. The harder the asphaltum or pitch the greater the tendency to stouten on ageing. This phenomenon may be illustrated by the viscosity figures of a solution of Rafaelite in petroleum hydrocarbon. Rafaelite may be regarded as a hard asphaltum.

Viscosity of solution initially	23 secs.
Viscosity of solution after 7 days	42 secs.

(Viscosities were determined at 25° C., using a Ford cup viscometer.)

Aromatic hydrocarbons are much better solvents for asphaltums and pitches than petroleum hydrocarbons. They yield solutions of lower viscosity for a given amount of solvent, with less tendency of gelation or stoutening. It is not always possible to use an aromatic hydrocarbon as the sole solvent in black lacquers, etc., because of its pronounced lifting power for films over which it is applied. For this reason, white spirit is the best thinner to use. Blends of white spirit with coal-tar naphthas can be used with advantage if the ratio of the component

thinners is carefully adjusted. As in many other examples included elsewhere, butyl alcohol, even in small percentages, is very effective in reducing the viscosity of asphaltum solutions. Other good solvents for asphaltums are the chlorinated hydrocarbons, turpentine and carbon disulphide, although the latter finds application only in analytical processes in the laboratory.

Instability of solution is shown sometimes by a complete or partial separation of the asphaltum. The asphaltum collects as a stiff jelly at the bottom of the container with a thin supernatant liquid. This liquid may contain enough asphaltum in solution to colour it, and a casual observation can create a false impression of solubility.

Some asphaltums, such as Manjak, are practically insoluble in white spirit and need special treatment to produce black compositions from them.

In Vegetable Oils.—In evaluating an asphaltum for use in products in conjunction with drying oils, its solubility in these oils must be critically examined. Petroleum asphaltums and natural asphaltums of the Gilsonite type dissolve readily by simple heat treatment irrespective of the ratio of oil to asphaltum. The two ingredients are heated to temperatures around 250° C., stirred until homogeneous, and the mixture cooled and thinned. No special care is necessary. The asphaltum may be fused first and the oil added gradually or the asphaltum may be fed into the hot oil. The former method is the more popular. The harder the asphaltum the stiffer the gel provided by the asphaltum-oil mixture, and the greater the quantity of thinner necessary to reduce it to workable viscosity. With oil present the tendency to stouten or gel on storing is still apparent. Unstable solutions may deposit a sludge of insoluble asphaltum.

Asphaltums like Manjak and Rafaelite need special treatment to effect solution in drying oils. Manjak is very difficultly soluble. A solution of it is obtained by first heating it with part of the oil only to 290°–300° C. It chars very readily and the blend must be kept stirred continually. The constant movement of the mass also helps the Manjak to dissolve. Further amounts of hot oil may be added on a good fire, maintaining the temperature at 290°–300° C. The heating and stirring is continued until all the soluble part of the asphaltum has gone into solution.

Manjak is rarely used alone as a solution in solvent. Whenever it is encountered, oil is generally present also.

Rafaelite needs similar heat treatment to incorporate it in drying oils. The cooking process is not so long and tedious as with Manjak, but the ratio of oil to asphaltum is limited. The most satisfactory method of incorporation is to heat the Rafaelite to 290°–300° C., and to add the oil previously heated to 250° C. in small amounts at a time, avoiding substantial reduction in temperature. If the oil has been correctly incorporated, a smooth pill should be obtained, in contrast with a seedy pill when solution is incomplete. A preliminary heat treatment of Manjak

or Rafaelite with an acidic resin such as rosin or run Congo at 300° C. for fifteen minutes, appreciably facilitates the subsequent incorporation of oil. Moreover, the presence of an acidic resin contributes to a marked degree to the stability of the resultant varnish.

Thus in testing asphaltums for solubility different methods must be used to accommodate the various types.

Insoluble Matter.—When examining for solubility, the percentage of insoluble material should be determined simultaneously. With petroleum asphaltums, Gilsonite, Rafaelite and Density asphaltum, the amount insoluble should be very low, and is generally negligible. With Manjak, however, considerable amounts remain undissolved, and these often vary in magnitude with different consignments. The amount of material insoluble in white spirit and/or oil is important, and manifests itself in several directions. The varnish maker is buying raw material which is valueless, and since the opacity of the final product is governed by the quantity of asphaltum in solution, this suffers also. For all but the first-class finishes, products based on Gilsonite or Rafaelite dissolve almost completely, and normally need no cleansing by centrifuging. Abnormal amounts of insoluble matter in these asphaltums would necessitate cleansing. Finishes containing Manjak contain so much insoluble matter that centrifuging is always essential. The difference between Manjaks is that in some there is so much matter undissolved that more frequent cleaning of the centrifuge bowl is necessary, which means a reduction in through-put.

The solutions obtained in white spirit or drying oil are flowed on to glass. A careful examination of the film by looking both directly at it and through it, reveals the presence of fine matter in suspension. Application of thick films should be avoided since they mask the presence of suspended matter.

The insoluble matter in suspension is often in such a finely divided form that it is impossible to remove it by centrifuging. This necessitates filtering, and may prove a serious disadvantage. An ash determination is a useful guide to the amount of insoluble mineral or other extraneous matter present.

Opacity.—Since most finishing compositions based on asphaltums or pitches rely solely on the presence of these materials for their opacity, this property should be the subject of test also. The comparative opacities of asphaltums can be determined by examining similarly constituted films on glass against a strong light.

Gloss.—In assessing asphaltums or pitches for gloss they should be judged by their performance in the precise finishes for which they will be used ultimately. Furthermore, they should be dried under the same conditions which they will encounter in use, thus black japans and Brunswick blacks would be air dried, and cycle enamels or insulating varnishes stoved.

Melting-Point.—Melting-point is a useful distinguishing constant. Asphaltums and pitches have no sharp melting-points. The melting

range is comparatively large, extending from initial softening to complete fluidity. A record of these two limits provides valuable information on the thermoplastic behaviour of the film, besides providing information on the possibility of thinning with certain solvents, and the minimum permissible temperature for thinning.

Many methods have been used for the determination of melting-points. The ring and ball method is the most popular, and consists in recording the temperature at which a steel ball falls through a ring, the aperture of which is plugged with the asphaltum. Other methods involve the use of mercury which is supported on the surface of the asphaltum. As the temperature is increased the asphaltum softens, and the temperature is recorded when the mercury subsides into the molten mass, or percolates through it until it runs away at the bottom. In one method the asphaltum forms a solid plug in the bottom of an open glass tube and a definite volume of mercury is held above it. The method due to Kramer and Sarnow is based on this principle. In another method (Schenk zu Schweinsberg) the mercury is supported by powdered asphaltum in a bent tapered glass tube. Mabery and Sieplein record the temperature when a specimen of asphaltum, projecting over the edge of a supporting platform, loses shape and flows from the platform. The heating of the specimen is derived from the surrounding air bath. Kovacs fills a metal cup with the asphaltum and records the temperature at which it flows through a small aperture in the base of the cup. Another method (French) consists in filling vertical tubes with powdered asphaltum. A weighted piston rests in the tube on the top of the asphaltum, and the temperature is taken when the piston falls, due to the contraction of the powder on melting.

The simple procedure of heating two pounds or so of asphaltum in a small varnish pot until quite molten, allowing it to cool, and noting the minimum temperature at which easy thinning is possible, is a useful and practical test. The temperature at which stirring of the mass is just possible may be determined also.

Hardness.—Hardness is determined by means of a penetrating machine or needle penetrometer. Results are based on the distance a needle penetrates vertically into a sample, under a standard load, in a given time, under specified conditions of temperature. Using an apparatus of this type, and conducting determinations at different temperatures, information is obtained on the relation between temperature and softening. Another method of assessing hardness consists in forcing a circular plunger through a specimen at a uniform rate. The weight necessary to accomplish this forms the basis of hardness comparisons.

Ductility.—Asphaltums or pitches have a pronounced tendency to exhibit brittleness at normal or lower temperatures, or to fracture on sudden impact. These properties are involved in bending tests for flexibility. Further information may be derived from tests for ductility. A test has been devised in which prisms of standard dimensions are sub-

jected to a longitudinal stress. The percentage elongation before breaking is taken as a measure of ductility. Determinations may be done at any convenient temperature. The standard method of the Institute of Petroleum involves the use of a test piece, dumb-bell shaped, of 1 sq. cm. cross-sectional area. In this instance the ductility is recorded as the elongation in cm. at the breaking point.

Chemical and Electrical Tests.—When asphaltums are to be used for certain purposes, special tests have to be carried out. These include tests for acid and alkali resistance, and for dielectric strength.

Durability.—Accelerated weathering tests have been devised, and one due to Strieter and Snoke consists in subjecting the film to arc light and water immersion alternately. The extent of degradation is followed by an examination of the wash water. The action of atmospheric oxygen in the presence of light promotes the formation of ketonic and acidic compounds.[14]

Adhesion.—Goldman has suggested a method of determining the adhesion of asphaltums and pitches to surfaces. When they are used alone as simple solutions it should provide useful information. Molten cups of the unthinned asphaltum are placed on the surface and allowed to cool. The force necessary to detach the cup from the surface is a measure of the adhesion. The maximum adhesion it is possible to measure by this method is limited by the tensile strength of the asphaltum.[11]

Analysis.—These materials are so complex chemically, and they possess such inconvenient physical properties that their chemical analysis or the performance of distinguishing tests is extremely difficult. Often the results are inconclusive. Some simple tests, however, do yield useful information sometimes. One valuable test for differentiating between natural or artificial bitumens and coal-tar pitch exploits a difference in solubility.

Solubility in Solvents.—The addition of petroleum benzine to a chloroform solution causes precipitation with coal-tar pitch but not with natural or artificial bitumen. In a method due to Kovacs and Sotet the bitumen is extracted with carbon disulphide. The resultant solution is poured into an excess of turpentine. When coal-tar pitch is present a light brown precipitate separates. No precipitate is obtained from a pure natural or artificial asphaltum solution. If desired the original carbon disulphide solution may be diluted with a large excess of absolute alcohol. The type of precipitate deposited furnishes the means of distinguishing between coal-tar pitch, natural asphaltum and petroleum asphaltums. The former yields a brown precipitate and the latter a fine black flocculent precipitate, whilst the natural asphaltum provides a black sticky mass.

The table on the following page shows the wide variation of the effect of white spirit upon the many types of asphaltums.

The malthenes or petrolenes of asphaltums are soluble in petroleum hydrocarbons but the asphaltenes are not.

A method of qualitative analysis of natural and artificial asphaltums and pitches, due to Heuber, involves solvent extraction in conjunction

with microscopic examination. A spot test is conducted with the following solvents: isopropyl alcohol, acetone, petroleum ether and carbon tetrachloride, in this order. It is claimed that differences in the speed of migration from the spot, as revealed by microscopic examination, provide clues to the identities of the asphaltums and pitches.[12]

Asphaltum or Pitch.	*Solubility in White Spirit.*
Gilsonite Density asphaltum Rafaelite Artificial petroleum asphaltums Wool grease pitch Stearine pitch	Soluble.
Drying and semi-drying oil pitches Bone pitch Blown artificial petroleum asphaltums	Partly soluble.
Manjak Cottonseed pitch Coal-tar pitch Wood-tar pitch	Insoluble.

Stain Number.—The stain number of asphalts is used to compare products from different sources. The asphaltum is placed between paper pads comprising many sheets of paper each. A given load is applied while the temperature is maintained at 130° F. Oil is exuded and the stain number is computed from the number of sheets discoloured by it.[13]

Effect of Sulphuric Acid.—The effect of fuming sulphuric acid on asphaltums and pitches produces characteristic results with different materials. The Durand-Clayé reaction involves the preparation of a solution of the specimen in carbon disulphide which is evaporated to dryness. Five c.c. of fuming sulphuric acid is added to 0·1 g. of the extract, the whole left twenty-four hours, diluted with 10 c.c. of water and filtered. The filtrate is diluted further with 85 c.c. water. The results obtained by Meinecke from this test are tabulated below:

Asphaltum or Pitch.	*Colour of Diluted Filtrate.*
Coal-tar pitch.	Black and opaque.
Brown coal-tar pitch.	Dark brown.
American asphaltum.	Pale yellow-brown.
Syrian asphaltum.	Yellow-brown
Trinidad asphaltum.	Yellow-brown.

An alternative method, due to Meinecke, consists in examining the supernatant liquid after shaking 0·1 g. of ash-free asphaltum, etc., with 10 c.c. fuming sulphuric acid.

Asphaltum or Pitch.	*Colour of Supernatant Liquid.*
Coal-tar pitch.	Greyish-black with green streaks.
Brown coal-tar pitch.	Grey, inclining to brown.
American asphaltum.	Brown, running into grey.
Syrian asphaltum.	Brown.
Trinidad asphaltum.	Brown.

Unsulphonated Residue.—Church[14] evolved a method whereby the distillate (b.pt. 315°–355° C.), obtained by heating the asphaltum or pitch, is sulphonated with sulphuric acid at 100° C. The percentage of unsulphonated residue indicates the type of substance under examination.

Asphaltum or Pitch.	*Percentage of Unsulphonated Residue.*
Mexican petroleum asphaltum	86
Gilsonite	85
Wood-tar pitch	0
Fatty acid pitches	0

Saponifiable Matter.—Depending upon the origin, variations in the amount of saponifiable matter arise. The following are completely, or almost completely, unsaponifiable: Gilsonite, Density asphaltum, Rafaelite, Manjak, artificial petroleum asphaltums, wood-tar pitch and coal-tar pitch. Types yielding substantial saponifiable matter are bone pitch, wool grease pitch and the stearine pitches.

Sulphur.—Of the elements which occur in asphaltums and pitches, sulphur is the only one which is normally of any interest to the varnish maker. Many methods of estimation involving fusion have been suggested, but these are open to the objection of possible inaccuracy due to volatilisation. One of the soundest methods is combustion in a current of oxygen. The products of combustion are absorbed by dilute caustic soda which is subsequently titrated.

Properties

Asphaltums and pitches perform the rôle of a resin or of a resin-oil mixture. The hard types with high melting-points behave as resins, and the softer types with lower melting-points as resin-oil mixtures.

All possess some degree of opacity, and for this reason they permit the formulation of black enamels without the addition of pigment.

Most of these materials are chemically inert. They show no tendency to attack metallic surfaces on which they are applied, or any tendency to be attacked by corrosive chemicals whether acid or alkali. Stearine pitches and similar pitches from vegetable sources are, however, susceptible to attack by chemical reagents by reason of their composition.

Asphaltums and pitches retain their gloss at high temperatures. Except for the few little used acidic types of pitches, pigments may be incorporated without regard for basicity.

They have excellent water resistance, and coal-tar pitches are claimed to be outstanding in this respect.[15] Bituminous products also possess good electrical properties, and this may be attributed in part, at least, to their excellent water resistance.

Durability is variable, depending upon the source of the asphaltum or pitch, but it can be improved often by the addition of mineral fillers. Strieter points out that the effectiveness is governed both by the size and type of filler.[16]

Defects

Incompatibility.—Asphaltums and pitches possess many defects which the ingenuity of the formulator has to overcome. Of these, the most important is probably their limited compatibility, and this, as elaborated elsewhere, varies with the source of the bituminous material. Even the most compatible types do not blend well with alkyds, pure phenol formaldehyde and urea formaldehyde resins, or chlorinated rubber. With chlorinated rubber, for example, adhesion is lost. Mixtures of bitumen and alkyd are deceptive. Initially, apparently perfect compatibility may be effected, but subsequent storage may result in complete separation. Blends with alkyds, therefore, should be studied carefully before embarking on large scale production. Unsatisfactory compatibility is also demonstrated when attempts are made to tint a varnish, by dissolving bitumen directly into it by warming. Due to the presence of thinner the temperature of solution cannot be raised much above about 120° C., and the bitumen has a tendency to break into small pieces only, without disappearing completely into solution. The only safe method of tinting is to add a previously prepared solution of bitumen to the varnish. Under these conditions it disperses satisfactorily.

Antioxidant Effect.—Asphaltums and pitches seriously interfere with the normal drying process of substances which dry by atmospheric oxidation. This makes the formulation of quick drying medium or long oil compositions containing them very difficult. The addition of as little as 5 per cent of asphaltum calculated on the other non-volatile constituents of the finish is often sufficient to delay the drying time by hours. The methods which are usually adopted to overcome this defect are to keep the content of asphaltum to a minimum, to subject it to a sweating process before incorporating the other ingredients, in order to distill off any volatile matter, to increase the proportion of good drying oil like tung oil at the expense of linseed oil, and to increase the amount of driers.

The amount of driers used in black air-drying finishes based on asphaltum is substantially greater than that in straight oleoresinous finishes. Lead drier is added in a predominating amount and manganese often exerts a surprising influence with this type of product. Cobalt is added also. The drying properties of black varnishes sometimes improve on ageing.

The antioxidant effect of bituminous substances can be exploited in stoving finishes which are prone to rivel, if colour is unimportant. One per cent of asphaltum, added to a copal stoving varnish with a slight rivelling tendency, completely eliminates it.

Gloss.—Asphaltum and pitches do not permit pigmentation without substantial loss of gloss. This is much more evident than with oleoresinous varnishes. Where gloss must be retained resins are added. Where pigmented bituminous compositions are used as undercoatings, loss of gloss is unimportant.

Staining Power.—Their strong staining power prevents their use in media for pigmentation with almost every pigment except black. Pale artificial petroleum bitumens, wood tar, or rosin pitches are pale enough for pigmentation with red, green, blue and brown pigments.

Bleeding.—By reason of their inertness most bituminous materials do not change fundamentally on exposure. Their initial solubility remains unaltered. This means that subsequent application of finishes over them containing mutual solvents, results in immediate attack and bleeding occurs. Black japans, for example, must be so formulated, that when varnishes are applied over them, the film resists attack. In cases where attack occurs the varnish assumes a greenish fluorescent appearance.

Solvent Retention.—Another defect is that of solvent retention. With air-drying bituminous finishes this phenomenon is very apparent.

Thermoplasticity.—Asphaltums and pitches are thermoplastic. Hot films which are sticky permit the adhesion of extraneous matter carried in the air, which causes unsightliness.

Application

Compositions derived from asphaltums and pitches are applied in a wide variety of ways. They may be brushed on or applied by coating machine. They may be sprayed at ordinary or elevated temperatures. The latter method of spraying is becoming more popular. Finishes which are very viscous at ordinary temperatures are warmed until they are reduced to spraying viscosity. Hot spraying methods have the advantages that loss of volatile matter is minimised, and what is probably more important is the fact that heavy films can be applied without risk of flow troubles. This latter advantage means that the result obtained by two ordinary spray coats is yielded by one coat only. Some metals, particularly when fabricated in certain forms, are difficult to coat with continuous films because of the tendency of the liquid film to "run away." Hot spraying minimises this tendency.

When application is made by dipping this is also conducted at ordinary or elevated temperatures. Hot dipping offers the same advantages as hot spraying. After immersion in the hot composition, the article is withdrawn and the excess removed by vigorous agitation. Pipes and other ironwork are coated by immersion in hot liquid bitumen. As soon as they have cooled to room temperature the bitumen sets hard. The articles to be coated may be heated before dipping, to avoid chilling of the hot material in the dipping tank. The addition of small amounts of rosin or vegetable oil greatly reduce the viscosity of the molten bitumen.

Uses

By reason of their cheapness and for other reasons, asphaltums and pitches have found application in compositions and varnishes for many purposes.

Simple mixtures of natural asphaltums and rosin form the basis of

Brunswick blacks, chassis blacks, and black lacquers for all kinds of ironwork. With carbon or vegetable black, Berlin blacks are obtained. Black japans, which are an improved form of Brunswick black, contain drying oil in addition to asphaltum and rosin or other resins.

Their property of water resistance is exploited in many waterproofing compositions. Digby records that for submerged objects they give up to ten times the protection of other paints.[17]

In this respect Kindscher suggests a combination of bitumen and chlorinated rubber. In view of the uncertain compatibility of these materials, however, they should be carefully chosen.[18]

Coal-tar pitch is said to be one of the best known waterproofing agents, and it is not surprising that it figures prominently in many formulæ. Bituminous compositions are used to prevent the swelling of wood. The bitumen may be plasticised with vegetable oils or their fatty acids as desired. Blends of coal-tar pitch and blown asphaltum are used to protect pipe lines against water. A primer with good adhesion for iron and steel, designed for use under coal-tar products, contains Gilsonite, another asphaltum, stearine pitch, fish oil and thinners.[15] Asphaltum compositions are used on concrete to prevent ingress or deterioration by sea-water. The composition is applied hot by vacuum impregnation.[19]

For the protection of buildings, Platzmann enumerates the following characteristics as being essential in a bitumen. Paraffin and naphthalene contents should be as low as possible. Tendency to crack or flow in the temperature range normally encountered should be absent. The bitumen should be at least almost completely soluble in carbon disulphide, and should have a volatile content when heated at 160° C. for five hours, of not more than 0·5 per cent.[20] Furthermore, the chemical inertness of bituminous products makes them particularly suitable for use on concrete or cement. When the plasticising constituent is a drying oil, this should be kept to a minimum, since it is the weakest part of the mixture for alkali resistance.

A waterproofing process for walls consists in first applying a mixture of coal-tar pitch and asbestos fibres. Over this is placed a layer of bituminised felt followed by a further coating of the pitch and asbestos.[21] Another application is for asphalt shingles. Stiff asphaltum-asbestos fibre plastics are used to stop cracks on roofs, valley gutters, etc. Another type of roofing compound consists of three parts of asphaltum and one part of oil-free mineral oil wax dissolved in a petroleum distillate.[22]

Varnishes based on bitumens are used as waterproofing finishes for tarpaulins, although for this, boiled linseed oil pigmented with vegetable black is still very popular.

A waterproofing composition for general use is made from a blend of coal tar, raw rubber, lead acetate, and slaked lime, the whole being adjusted for viscosity as required by the addition of thinners.[23] Considerable quantities of artificial bitumens from petroleum are used for impregnating paper and fabric to confer waterproofness.

The interiors of iron water tanks are often protected with bituminous coatings, and concrete reservoirs are protected similarly. With the latter, either the composition itself fulfils the function of water retardant, or it acts as an intermediate coating between layers of bituminised felt.

The waterproofness and general impermeability of asphaltums and pitches prompts their choice for anti-corrosive paints for iron or steelwork. Corrosion of steel, according to Kindscher, depends upon several factors, among which may be included the type of immersion whether intermittent or continuous, the effect of the motion of the water, the abrasive action of sand, the growth of organisms and the composition of the water. Asphaltums chosen, therefore, for the protection of steel must withstand all these influences, and in addition must be resistant to atmospheric oxidation, possess good adhesion, and be effected as little as possible by sudden temperature changes.[24] Carefully selected bituminous materials fulfil all these functions satisfactorily.

Good protection against corrosion for Russian oil pipe lines was given by bituminous products containing fillers such as talc and asbestos.[25] Another composition for pipes consists of a blend of raw or oxidised artificial petroleum bitumen with a solution of paraffin wax in spindle oil. The paraffin wax solution can be substituted by petroleum jelly, and powdered asbestos may be added also.[26] Processes have been described for the protection of pipes, wherein the pipe is covered with successive layers of bitumen and sheet fibrous material. The introduction of leafing pigments like graphite or aluminium greatly increases the imperviousness of bitumen films, and consequently their anti-corrosive properties.

In spite of the excellent water resistance of coal-tar pitch Van der Veen condemns its efficacy, when unmodified, on pipes in aggressive soils. He emphasises the importance of non-porous continuous films, and suggests that film porosity can be determined electrically.[27]

Natural or artificial bitumens, by reason of their low acidity, form very satisfactory media for metallic paints. Since the essential properties vary appreciably, each bitumen should be tested carefully for suitability. The lustre and general appearance of the film depend also on the aluminium powder, which may vary considerably for leafing properties. There is a tendency for the natural dark colours of the bitumens to upset the brilliant metallic lustre of the aluminium flakes, but this can be reduced by selecting a pale or light bitumen. Not only does the introduction of aluminium powder increase the water resistance as indicated already, but it confers chemical resistance also. Good resistance to hydrochloric acid gas, and steam charged with phosphoric acid, has been reported.[28] Heat reflecting surfaces for roofs are made by applying a bituminous varnish, and whilst it is still in the tacky state, aluminium powder is dusted on or sprayed on as a dispersion of aluminium paste in petroleum hydrocarbon.

Because of their non-drying and thermoplastic properties asphaltums and pitches make valuable adhesives. The harder grades may be softened

by the addition of softer grades, mineral and vegetable oils, rosin oil, etc. Adhesives are used by applying the composition to the surface, either as a cold solution containing thinners, or as a hot liquid free from volatile material. With the former it is necessary to allow the thinners to evaporate before a tacky state is reached. With the latter the adhesive may lose its tackiness on cooling so that rapid application of the second surface is necessary before this occurs. Alternatively, the adhesive is designed to remain sticky at room temperature. Another method of using a bituminous adhesive in which use is made of its thermoplasticity consists in applying a heavy coating to the two surfaces to be joined. The films are allowed to dry, heated to reproduce stickiness and, whilst in this state, pressed together. On cooling, the two surfaces are firmly cemented. An adhesive for fixing bituminised sheets to surfaces consists of hard oxidised bitumen, fifty parts, white spirit or naphtha, forty-five parts, and creosote, five parts.[30] Bitumens figure prominently in black mica sticking varnishes.

For high temperature black stoving enamels for motor car wings, cycle frames, and accessories, natural asphaltums are unsurpassed. The high stoving temperatures used, 400°–500° F., give exceptionally hard glossy adherent films. Gloss retention of the asphaltums at elevated temperatures makes this possible.

Asphaltums and pitches have good heat resistance and form the basis of many paints and lacquers for smoke stacks, boilers, exhaust pipes and radiators. With chlorinated diphenyls they are incorporated in fire resisting compositions of which the following are examples: blown asphalt, three parts, is mixed with montan wax, one part, and chlorinated diphenyl, six parts; Mexican asphalt or stearine pitch, four parts, is mixed with chlorinated diphenyl, six parts; or a blend of Gilsonite and montan wax, four parts, is mixed with six parts of chlorinated diphenyl.[31]

Good electrical insulating properties have prompted their incorporation in every type of black insulating varnish, whether for the production of Empire insulating cloths or for the impregnation of coils, rotors or transformers. Other electrical uses are as sealers for accumulators and condensers.

A solution of bitumen in paraffin with some resin is used as a binder for sand in foundry cores.[32]

Another interesting application is in the production of sound deadening spraying compositions for motor car bodies. A typical example comprises Gilsonite, eleven parts, petroleum asphaltum, twenty-three parts, linseed oil, two parts, agalite, fifteen parts, long fibred asbestos, fifteen parts, and naphtha, thirty-four parts.[33]

Other uses include the manufacture of binders for coal briquettes, printing and photogravure inks, and as modifying agents for rubber.

Much interest has been aroused lately in the production of bituminous emulsions, the bulk of which has been absorbed in camouflage paints for spraying. Apart from obvious advantages such as saving of volatile thinners, emulsions are useful in that they may be applied directly to damp surfaces.

CONSTANTS OF ASPHALTUMS AND PITCHES

Asphaltum or Pitch.	M.Pt. or Range (° C.).	S.G.	% Ash.	% Sulphur.
Gilsonite	135°–205° (142° C.)*	1·044–1·076	0·75	
Manjak—				
Barbadoes	145° (120°–175°)	1·10–1·15	3·0	0·8
Trinidad	220°			
Origin unknown	168°	1·14	0·1	
Syrian asphaltum	120°	1·11	0·01	6·0
Impsonite	does not melt	1·10–1·25		
Grahamite	175°–315°	1·15–1·20		
Colombian asphaltum	135°			
Rafaelite	180° (176° C.)*	1·10	0·2	2·3
Rosin pitch	70°			
Bone pitch	70°–100° (98° C.)*			
Wood-tar pitch	190°			0·0
Petroleum asphaltic Bitumens—				
Californian	40°–105°	1·05	0·05 +	—
Trinidad	55°–100°	1·00	0·5–1·3	2·5
Mexican	60°–120°	1·01	0·05 +	4·6
Stearine pitches—				
Lard pitch	45°	1·00		
Tallow pitch	85°	1·06		
Wool grease pitch	30°–35°	1·02		0·0
Whale oil pitch	38°	1·02		
Cottonseed pitch	30°	0·95		
Palm oil pitch	75°	1·03		
Coal-tar pitch	35°–175° variable †	1·25		0·3
Lignite pitch	85°			2·1

Authority: Morrell, "Varnishes and their Components," and other sources.

* Ball and ring determinations on current supplies.

† Commercially available products rarely possess melting-points above 105° C.

Other Petroleum Products

The products for consideration are the linseed oil or linseed oil-resin substitutes, which are known under the names Firnagral 1 and 2 and Iranolin. Firnagral 1 was produced originally in Germany. Firnagrals 2 and FL are produced in this country. Iranolin is a product of the Anglo-Iranian Oil Co. Ltd.

All these materials are dark brown viscous oils, and thus cannot be used with light colours, although they have good wetting and dispersing properties. Very little information has been published concerning their methods of production. It is believed that Firnagral is derived from the oxidisable portion of crude petroleum, and consists of aromatic cyclic hydrocarbons. Iranolin is also aromatic in character.

Although these materials are stable, the addition of cobalt drier causes drying to occur. Cobalt is preferable to lead and manganese for this

purpose. By comparison with linseed oil the dry is slower. Twenty-four hours or more are necessary to attain the hard dry state.

Both Firnagral and Iranolin show up best in mixtures with vegetable drying oils and resins, when more rapid drying is attained.

Compatibility is good. Satisfactory blends are made with treated and untreated vegetable oils, mineral oils, natural resins such as run Congo and rosin, and with other resins such as phenol formaldehyde resins, alkyds and rosin ester. Iranolin is claimed to dissolve rubber, and Firnagral has been suggested as a plasticiser for chlorinated rubber.

The chemical resistance of Firnagral and Iranolin is good, and their use in compositions for concrete and cement is indicated. Water impermeability and durability are good also, and both products form the basis of anti-corrosive paints for iron and steel. Firnagral can replace linseed oil in putty, and in this respect small additions of chlorinated rubber are advantageous.[34] It may also replace rosin oil in news inks.

	Firnagral FL.	Firnagral 2.	Iranolin.
Specific gravity . .	1·026	0·9495 (60° C.)	1·015
Viscosity . . .	7450 (Redwood 1 at 60° C.)	526 secs. (Redwood 1 at 60° C.)	85 contipoises (94° C.)
Boiling range . .			240°–400° C. (10 mm.)
Flash-point . . .		420° F.	
Refractive index . .		1·5410 (50° C.)	
Ash	0·026 %		
Acid value (as acetic acid)	0·267 %		
Sulphur content . .	0·79 %		
Iodine value . . .	52		

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CHAPTER 13

WAXES

A CHAPTER devoted to waxes, in a volume of this type, may appear, at first sight, to be unnecessary. Although waxes are not used in substantial quantities in varnish manufacture, by comparison with other raw materials, their inclusion is essential to obtain certain effects. Furthermore, there has been a certain amount of overlapping into the wax polish trade.

For convenience, waxes will be considered under two heads only, natural and synthetic. In the section devoted to natural waxes will be included all waxes derived from natural sources, even if they receive considerable process treatment. Synthetic waxes will include those waxes which are synthesised from basic raw materials by chemical reaction, and those proprietary brands whose methods of preparation have not been publicly divulged.

Among the outstanding characteristics of waxes which distinguish them from other varnish ingredients are their comparative chemical inertness, solvent retention, and insolvency in most organic solvents.

NATURAL WAXES

Paraffin Waxes

These are used to a greater extent than any other wax, whether natural or synthetic. Their cheapness is probably the controlling factor of their popularity.

Paraffin waxes are obtained from crude petroleum by distillation, the amount present varying considerably with the source. Petroleum from Burma is rich in wax, and other sources are Assam, East Indies, North Africa, Timor, U.S.A., Mexico, Canada, Russia, Rumania and Galicia. Paraffin waxes are also obtained from lignite and shale.

Paraffin waxes are chemically inert substances, consisting of mixtures of hydrocarbons corresponding to the C_nH_{2n+2} series. They vary in colour from pale yellow to water white, and most commercial grades encountered in the varnish trade are the latter variety. Melting-point varies from about 35° to 77° C., and hydrocarbons corresponding to the formulæ, $C_{23}H_{48}$, $C_{24}H_{50}$, $C_{25}H_{52}$, $C_{26}H_{54}$, $C_{28}H_{58}$ and $C_{29}H_{60}$ with melting-points covering the range 48° to 63° C. have been isolated.[1] The following grades of wax are available, and are distinguished by their melting-points: 38°–46° C., 46°–48° C., 48°–49° C., 50°–52° C., 63°–65·5° C. and 71°–74° C. Price usually increases with melting-point. The most popular grade is that melting at 50°–52° C. Grades with lower melting-points than this present storage difficulties, for being supplied in hessian bags they slowly lose shape in warm weather and matt together.

Paraffin waxes possess good solubility in both aliphatic and aromatic

hydrocarbons in hot solutions, and although they dissolve in cold hydrocarbons their solubility usually amounts only to a few per cent. Harrap and Evans [39] have given the solubility of paraffin wax (m.pt. 50°–52° C.) in a range of petroleum fractions at 15° and 25° C., and these are included in the table below:

SOLUBILITIES AMERICAN 122–5 WAX

(*Gm. wax/100 ml. solution*)

Temp., °C.	S.B.P. 1	S.B.P. 2	S.B.P. 3	S.B.P. 4	S.B.P. 5	S.B.P. 6	Rubber Solvent	White Spirit
15	14·1	12·3	9·7	13·5	9·7	9·2	9·6	8·9
25	24·1	23·8	23·0	23·6	22·8	22·3	22·5	20·1

Aromatic hydrocarbons are better solvents than aliphatic hydrocarbons, thus, if possible, paraffin wax should be added to varnishes thinned with xylol, toluol or naphtha, in preference to those containing white spirit, paraffin, or benzine. Esters and alcohols are poor solvents, the wax only possessing slight solubility even in hot alcohol. Paraffin wax dissolves in hot solutions of most oleoresinous or synthetic varnishes, almost irrespective of the ingredients. Thus it is soluble in varnishes, containing white spirit, naphtha, turpentine, linseed, castor, perilla, tung and stand oils, run copals, damar, rosin, rosin and copal ester, phenolic and maleic resins, and alkyds. On cooling to normal temperatures, however, a considerable quantity of wax crystallises out. If it is desired that the wax remains permanently in solution in the varnish, not more than 1–2 per cent should be present, and this amount is usually sufficient to yield the properties desired. The lower the melting-point of the wax the greater the chance of its retention in solution in the varnish.

Wax does not crystallise rapidly from varnishes if present slightly in excess of the limits suggested. After the varnish has cooled to atmospheric temperature, several hours up to one day may elapse before separation occurs. Separation of solid wax crystals is a serious drawback, for they induce cissing during stoving. Such products should be tested, therefore, for crystallising tendency, by subjecting them to temperatures lower than those which will be reasonably encountered on storage.

An important feature of paraffin waxes is that they can be continuously heated without degradation or serious loss of colour.

The flexibility of paraffin wax can be improved by small additions of rubber. Additions of 0·25 to 2 per cent are suggested.[2] Other modifications of paraffin wax have been recorded, yielding improvements in properties. Treatment above 100° C., with metallic compounds like the aluminium salts of fatty acids possessing more than five carbon atoms, yields a processed wax with a higher melting-point and viscosity, and it possesses better solubility in organic solvents.[3]

Holde has devised a simple test for the detection of unsaponifiable waxes in vegetable oils. Six to eight drops of the oil are boiled for two minutes with 3 c.c. of N potassium hydroxide. Up to 10 c.c. water is added slowly. Unsaponifiable substances cause turbidity, exceptions being spermaceti and bottlenose oils.[4]

Mineral Jelly

Mineral jelly is a petroleum product and a typical example is vaseline. It is a soft substance with a melting-point of about 30° C. It varies in colour, depending upon the extent to which it has been bleached, from a very pale straw to a golden-yellow. Mineral jelly also exhibits a characteristic bluish fluorescence. It may be regarded as a mixture of paraffin wax and heavy oils.

It is not used to such a great extent as paraffin wax, probably because it does not separate from solutions, when required, in crystalline form.

Beeswax

Beeswax is obtained from honeycombs by melting in hot water. Apart from the English beeswax, the wax is produced in Portugal, Portuguese Africa, East Africa, Canada, India and other sources.

It is a complex mixture of esters, acid, alcohol and hydrocarbon. The chief ester is myricyl palmitate, and the alcohols ceryl and myricyl with cerotic and melissic acids.

Beeswax has a characteristic and very pleasant smell.

The appearance of the commercial wax varies considerably, according to the grade, of which there are many. It varies from a dark brownish soft wax to a hard white or bleached wax. The physical condition of the wax is governed by the source, the care taken in separation and the subsequent refinement.

The molten wax from the combs is strained. It is refined, normally, by one or combinations of two methods, namely, repeated boiling with water or bleaching. The latter process is accomplished either naturally by means of sunlight or by chemical means. The chief chemical bleaching agents are potassium permanganate and dichromate, hydrogen peroxide, or ozone.

Buchner segregates beeswaxes into five different types. The first type includes all waxes possessing constants within certain specified limits. These are designated as normal. The second type includes waxes with constants slightly outside the limits, such as wax from East Africa, or wax obtained by extraction with an unsatisfactory solvent. The African wax would be characterised by an abnormal amount of ceryl alcohol and hydrocarbons. In the third group he places Indian wax, with constants widely divergent from those of normal wax, particularly a low acid value.

Into the final two groups fall waxes whose condition has been modified by heat treatment. One includes waxes which have been heated above 150° C., and the other, waxes with a heterogeneous composition caused by rapid cooling.[5]

The luminescence produced in ultra-violet light has been suggested as a means of assessing the purity of beeswaxes. A pure wax is stated to appear light grey, and adulterated waxes as dark brown.[6] Beeswax emulsifies readily.

Lanolin

Lanolin is included in this chapter for convenience of reference.

In appearance, lanolin, wool grease, or wool wax, is between the vegetable oils on the one hand, and the true hard waxes on the other. It is a soft material of mineral jelly consistency.

Lanolin is the natural grease of sheep wool, obtained either by solvent extraction or by alkaline treatment. In the latter case the lanolin is regenerated on acidification. Special grades of lanolin are obtained by distillation.

Lanolin appears to consist of a mixture of esters, like lanocerin, and alcohols like cholesterol and isocholesterol.

Commercial grades vary considerably from a dark brown evil-smelling grease to a pale straw product with a slight pleasant odour, used in toilet and pharmaceutical preparations.

Lanolin keeps well on storage. Lipson extracted wool wax from sheep fleece with ether, and examined it after two years' storage. Apart from a reduction in iodine value from 33·5 to 26·7 no substantial changes occurred. Acid and saponification values, for example, were practically unchanged.[7]

Lanolin has great affinity for water, and most commercial grades contain substantial amounts. The presence of water causes opacity which diminishes with the water content. So-called anhydrous lanolins are available for special purposes.

Because of its affinity for water, lanolin readily emulsifies. It possesses good solubility in aliphatic and aromatic hydrocarbons, and is compatible with many varnish constituents, including vegetable oils, run natural copals, rosin, coumarone and chlorinated rubber.

Ozokerite and Ceresin

This material is mined, and occurs in many parts of the world. The chief source is Galicia, but it is found also in the United States of America (Utah), South Africa, Egypt, Jugoslavia and Austria.

Its hardness and colour are variable. Some grades are soft, whereas others are appreciably harder, depending upon the source. Colour varies from a dark brown to an opaque pale straw. When specially refined it is sold under the name Ceresin. Ozokerite may be refined by vacuum steam distillation.

Ozokerites are not quite so inert as the paraffin waxes, as shown by a greater tendency to decomposition by heat, and in their sensitivity to sulphuric acid. They are also less soluble in petroleum hydrocarbons. Ozokerite has a lower solvent retention than paraffin waxes. In varnish

compositions, ceresin can be replaced often by a paraffin wax of similar melting-point without detriment. In fact, its constituents are chiefly hydrocarbons. Some so-called ceresin waxes are substantially hardened paraffin waxes.[8] Ivanovzsky states that normal and isoparaffins are present with resinous and asphaltic petroleum products.[9] Other workers claim to have isolated cyclic hydrocarbons. After homogenisation, natural German Ozokerites compare favourably with the best Polish grades for quality.[10]

Ozokerite substitutes, under the names amorphous wax and petroleum ceresin, are obtained from the distillation residues of certain American crude oils after solvent treatment.

Ozokerite is frequently adulterated with montan and paraffin waxes.

Montan Wax

Montan wax may be described as a bitumen wax. It is obtained from lignite by extraction with solvents, satisfactory solvents being petroleum hydrocarbons. The bulk of montan wax is obtained from bituminous brown coal, by extraction, in German Sudetenland. Before extraction the lignite is dried to reduce the water content. When this falls below 15 per cent it is extracted with benzene. Another method fixes the maximum water content permissible, before extraction, as 25 per cent, and in this instance a mixed solvent, consisting of benzene or toluene with the water immiscible portion of fusel oil or wood spirit, is used with advantage. The yield of wax extracted is about 30 per cent more than that obtained using benzene.[11]

The crude wax is a hard, brittle, dark brown or black substance, and exhibits a conchoidal fracture when broken. It is refined either by treatment with acids such as sulphuric or nitric acids, or by vacuum and steam distillation. Sometimes a mixture of potassium dichromate and sulphuric acid is used.

Among the constituents present is the saturated fatty acid, montanic acid, and an unsaturated hydrocarbon. Crude montan wax contains, in addition, about 30 per cent of asphaltic and resinous substances.

Since paraffin wax is used during the refining process with sulphuric acid, some of this wax may be present in the final product.

Montan wax has been modified in many ways, and is the basis of certain synthetic waxes. Details are given of montanin wax, derived from montan wax by neutralising part of its free acid with soda. Montanin wax has a melting-point of about 97° C., which is substantially higher than that of the parent wax.[12] More details are available, of the process of making waxes of higher melting-point by neutralisation, in the following examples. Montan wax is heated with 1 per cent of a metallic oxide, hydroxide or carbonate, in the presence of water, at temperatures of the order of 100° C. Suggested metallic compounds are lime, sodium hydroxide or potassium carbonate. An alternative method involves reacting the wax with the metallic compounds in a solvent at higher

temperatures (200° C.).[13] The formation of metallic soaps from the free fatty acids in the wax causes a viscosity increase also.

Specially prepared montan waxes are claimed to be superior to carnauba wax for certain purposes. Montan wax gives better continuity of film from liquid dispersions, binds turpentine and benzene more effectively, has greater solvent retention, and in some cases permits greater solvent dilution.[14] The high percentage of organic acids present enables montan waxes to be readily emulsified.

Peat Wax

Peat is available in many parts of the world, including Great Britain, Ireland, Canada, Finland, Russia and New Zealand. The wax is obtained by solvent extraction of peat, and figures given by Ivanovzsky for the amounts of extracted wax vary from 8 to 50 per cent, depending upon the origin of the peat.[15] Although it is but little used as yet, the similarity of peat wax with montan wax suggests that it might be a satisfactory substitute for it.

Carnauba Wax

This wax is a product of Brazil, and occurs as a powdery substance on the leaves of the palm tree. It is scraped from the leaves and melted in hot water. Bleached grades are available, the bleaching being accomplished by activated earths such as fuller's earth or potassium dichromate. Ivanovzsky emphasises that during refinement of carnauba wax, bleaching is accompanied by both substantial physical and chemical changes. According to Sturcke, carnauba wax is composed of esters derived from the following alcohols and acids: myricyl and ceryl alcohols, a dihydric alcohol ($C_{25}H_{52}O_2$), with carnaubic and a hydroxy acid

$$(C_{19}H_{38}CH_2OH \,.\, COOH).$$

A hydrocarbon, free cerotic acid and free myricyl alcohol have also been found.

Carnauba wax is extremely hard and brittle, and when heated has a pleasant characteristic smell. It varies considerably in colour, depending upon the grade, of which bleached, yellow, fatty grey and chalky grey are the commonest.

Ouricuri Wax

This is known also as Ouricoury wax, and is derived from the leaves of the ouricuri palm of Bahia. It is another palm wax varying in colour from pale to dark brown. When broken the fracture is conchoidal. Of the commoner waxes carnauba possesses the highest viscosity, but ouricuri wax has an even higher viscosity. The order of viscosity decrease as given by Ivanovzsky is ouricuri, carnauba, candelilla and esparto.[16] The presence of resin in the wax affects its viscosity, and generally, waxes refined by deresinification show diminished viscosities. The order of oil

absorbing capacity is similar to the foregoing except that carnauba displaces ouricuri with maximum capacity.

Ouropardo Wax

This wax is characterised by its high specific gravity of 1·23 and by the fact that it does not melt on heating, apparent resinification occurring. It is a yellowish-grey wax with an odour when warmed not unlike that of carnauba.

Candelilla Wax

Candelilla wax is a product of Mexico and Texas, and is obtained from plant stems by solvent extraction or by boiling with water.

Its precise composition has not been established, although a hydrocarbon, hentriacontane ($C_{30}H_{62}$), is said to be present.[17]

The wax is hard and may be a brownish-green colour, although other sources describe the colour as ranging from pale yellow to yellowish-brown.

Lowe states that candelilla waxes contain from 3–7 per cent of water, which can be removed by heating to 105° C., with simultaneous darkening. Heating at higher temperatures causes more pronounced darkening as the result of oxidation.[18]

The wax can be emulsified fairly easily.

Esparto Wax

Esparto wax is a hard wax, varying from light to dark brown in colour, similar to candelilla wax in some respects, and produced from esparto grass native to North Africa and Spain. During the preparation of esparto fibre for paper manufacture the wax is eliminated as a by-product. On breaking it reveals a conchoidal fracture. It can be emulsified if desired. It is sometimes used as a substitute for carnauba wax.

Insect Wax

This is native to China, and is sometimes known as Chinese wax. It is obtained from twigs and branches either manually or by hot water.

Ceryl cerotate is the chief constituent.

Spermaceti

This wax is derived from fish oils such as sperm, bottlenose and dolphin oils.

It is water white in colour, and is brittle and crystalline.

Cetyl palmitate is the chief constituent.

Shellac Wax

This wax is a by-product of the shellac industry wherein it is obtained from dewaxing processes. It is a fairly hard wax, but has little application in the varnish trade.

Japan Wax

Strictly speaking, this substance should not be considered under waxes, for it consists entirely of glycerides. Although it is correctly classified as a fat it is included for completeness. It is derived from the berries of trees cultivated both in Japan and China.

Refined grades are obtained by melting and sun bleaching.

It consists chiefly of palmitin, with small amounts of palmitic and japanic acids.

Because of the ease with which it emulsifies, Japan wax is a popular constituent of this type of composition.

Synthetic Waxes

Chlorinated Naphthalenes

These are produced in several grades by the chlorination of naphthalene, under the names of Seekay, Halowax, Nibren and Haftax. They vary in colour from black to a pale yellow, according to the degree of refinement. For special electrical purposes an almost white grade is produced.

The chief differences between these chlorinated products and the natural waxes are the higher specific gravity, melting-point and solubility of the former, which possess, in addition, the valuable properties of non-inflammability and excellent chemical resistance. These waxes are practically odourless.

Melting-points of the order of 120°–125° C. are possible.

The solubility of natural waxes in solvents at ordinary temperatures is restricted to a few per cent of wax. Chlorinated naphthalenes have excellent solubility in ordinary and chlorinated hydrocarbons, being as high as 170 gm. per 100 g. of benzene, 125 gm. per 100 gm. of trichlorethylene, 35 gm. per 100 g. white spirit, and 1·5 g. per 100 g. of industrial alcohol.

The alkali resistance of these waxes is indicated by the results obtained with Seekay wax R. 93. After immersion in caustic soda solution (7 per cent) for 500 hours at 17° C., the loss of chlorine amounted to only 0·0034 per cent, or to 0·024 per cent after thirty hours' treatment at 100° C. In consideration of their chemical constitution, their inertness is not surprising. Prolonged heating does not cause appreciable disintegration. No corrosion occurs between the waxes and metals. Tests conducted on aluminium, brass, copper, iron, stainless steel, monel metal and zinc, by immersion in the wax at 120° C. for 168 hours showed negligible penetration.

If desired, the waxes may be emulsified.

Chlorinated naphthalenes are compatible with natural waxes, bitumens and chlorinated rubber.

Like most chlorinated hydrocarbons they possess a certain toxicity. The chief risk occurs when these waxes are in the form of vapour or dust.

Inhalation of the vapours should be avoided, since serious results may occur. Externally, inflammation of the skin may be caused.

Chlorinated Paraffin Wax

Under certain conditions paraffin wax may be reacted with pure chlorine to yield highly chlorinated compounds. Chlorowax is a typical chlorinated paraffin wax available in commercial quantities.

Chlorination, as might be expected, produces profound changes in properties of the original wax. A yellow or amber colour is assumed, melting-point and specific gravity increase substantially, and solubility and compatibility show remarkable improvement. A chlorinated paraffin containing 43 per cent chlorine is liquid ; at 60 per cent chlorine content, a soft solid resin is produced, and at 70 per cent chlorine content the product is a brittle resin.

Chlorowax, containing approximately 70 per cent of chlorine, and possessing a molecular weight of about 1,160, is soluble in both aliphatic and aromatic hydrocarbons, ketones, drying oils, etc., and is compatible with a wide range of other varnish and lacquer constituents. It is compatible with alkyds, urea formaldehyde, polystyrene and vinyl resins, and ethyl and nitrocellulose.

Chlorination destroys the usual waxy characteristics of the starting material, and the resultant product becomes resinous.

Chlorinated paraffin waxes are claimed to be chemically inert, and non-toxic. Their chief application seems to be in the manufacture of moisture proof, fire retarding compositions.

I.G. Waxes

There is not much information available on the composition of these waxes, although OP wax is stated to be substantially the glycol ester of montan wax acids to which other substances have been added to increase colloidal properties and melting-point.[19] Z wax is said to be a high molecular weight aliphatic hydrocarbon. Oxidised montan wax is stated to be the basis of some of these waxes. The ash content is also significant.

Certain of these waxes have exceptionally high viscosities and are even more viscous than ouricuri wax.

Apart from consistency of quality, which the makers claim, as opposed to the irregularities which sometimes occur with natural waxes, the following properties of individual I.G. waxes are recorded :—

O and OP.—These are pale coloured, and have high melting-points. When broken they exhibit a conchoidal fracture. Because of their exceptional colloidal behaviour they absorb and retain large amounts of solvents.

E.—This is a pale yellow crystalline wax, recommended for use in emulsions.

S.—S wax is characterised by its high acidity, a property which is valuable in the production of emulsions. It is a very pale, hard, crystalline material.

CR.—This is a dark, easily emulsified wax.

B.—B wax is obtained in two forms—unbleached and bleached, the former being pale yellow and the latter ivory white. They are soft and easily emulsified.

New.—This is a very pale, almost white, soft wax. It is designed primarily for the production of emulsions. In fact, emulsions may be prepared by agitation in hot water without the addition of an emulsifying agent.

V.—Although this wax has a comparatively low melting-point it is very hard. It is an opaque white product, characterised by outstanding solubility in turpentine and petroleum hydrocarbons.

Z.—I.G. wax Z is odourless, tasteless and colourless. It has good hardness and chemical inertness.

Lanette Wax

Lanette wax is really a high molecular weight fatty alcohol. It is sometimes described as stearyl alcohol, although, in fact, it is a mixture containing also cetyl alcohol, obtained by hydrogenation of commercial stearic acid. The hydrogenation reaction is represented by the following simple equation :

$$R\,.\,COOH \xrightarrow{H_2} R\,.\,CH_2OH.$$

This wax is soluble in alcohols and hydrocarbons.

Lanette Wax SX.—This is a fairly hard wax-like substance varying in colour from white to yellowish. It is produced from the intermediate Lanette wax described above by partial sulphation. It is completely chemically compatible with vegetable oils, natural and synthetic resins, and solvents.

For the production of O/W emulsion paints containing synthetic resins, this wax is especially recommended.

Other Synthetic Waxes

These are produced by a variety of methods, and a survey of published information reveals the following :

A waxy product is obtained by emulsifying linseed oil with aqueous barium hydroxide.[20]

Beeswax substitutes are made by oxidising aliphatic petroleum hydrocarbons. The resultant products contain acids and esters, and usually possess melting-points in excess of those of the natural waxes.[21]

Other synthetic waxes are made by heating boric, boric-acetic, arsenious or phosphorous acids, with compounds of high molecular weight containing hydroxyl groups. Alcohols from the reduction of carnauba wax have been used.[22]

Modified waxes are yielded by treatment of beeswax or other waxes, and show improvement in colour, melting-point, solubility and unsaponifiable content. In an example, beeswax 600 parts is mixed with a catalyst 50 parts, and hydrogenated at 200° C. and 150 atmospheres pressure. The catalyst comprises one part of nickel to four parts of kieselguhr.[23]

The glycol, diglycol and glycerol esters of stearic acid have also been used as waxes.

Paraffin waxes and waxes resembling ozokerite have been synthesised by a modification of the Fischer-Tropsch process involving the use of water, water gas and coal.

Synthetic waxes are made from diphenylamine. Cases of dermatitis have been reported as the result of using them.[24]

Uses

Waxes are used in a large number of products of the varnish factory, or in products closely allied to them.

Paint Removers.—Probably their most important use is in the manufacture of paint removers where they perform two important functions. Firstly, they provide the material with a viscosity which enables it to be applied to vertical surfaces without undue flow, and secondly, they inhibit the evaporation of the solvents. The final viscosity of the paint remover depends upon the crystalline form of the separated wax, and on the type of structure set up, both depending upon the solvents and waxes present. Solubility of waxes varies considerably with temperature, and a remover must be carefully formulated if viscosity is to be maintained during hot summers without yielding unworkable products during the winter.

The wax must be chosen also so that when it separates from the solvent mixture, crystals float to the surface and orientate themselves in the form of a continuous film, which keeps the solvent locked beneath it. Further, the solvent retention properties of the wax should be carefully considered.

Waxes commonly used in paint removers are paraffin and ceresine.

Matt Finishes.—The insolubility of waxes is exploited in matt finishes. These rely for their mattness on the fact that most waxes are practically completely insoluble in the non-volatile portions of varnishes. The ideal matt varnish would be a clear product, which could be applied evenly and smoothly to a surface, attaining a velvet mattness gradually as the thinners evaporate. The waxes must separate in a finely divided condition, since large agglomerations of crystals result in unsightly films. If there is a tendency for the wax to separate from the varnish itself, the formula should be adjusted to ensure that a separation of fine particles only occurs. Large crystal formations are not always dispersed during brush application and a film of rough texture results.

The waxes most commonly used in matt varnishes are beeswax, paraffin, and sometimes ceresin.

Waxes have certain properties which are undesirable in matt varnishes. They inhibit dry by preventing evaporation of solvents, and also by protecting the film from free access to the air at the surface.

For this reason they are used cautiously, and often they are responsible for the mattness, in part only, other matting agents being incorporated.

In Stoving Varnishes.—The main function of wax in this type of material is to provide apparent surface hardness of film or "slip." The wax at the surface of the dried film seems to remove any residual tack to a large extent. Apparent hardness is conferred simultaneously, but this might be due to the slipperiness of the surface, preventing the ready incision of a knife blade, finger nail, or stamping tool.

Solid particles of wax in a varnish may cause cissing or pin-holing on stoving. The wax crystals melt on the application of heat and the surrounding varnish tends to recede from them.

In such compositions, therefore, type of wax, amount of wax, and composition of solvent mixture, must be carefully chosen to avoid this trouble.

Carnauba, paraffin and ceresin have been used successfully in stoving varnishes.

Waxes are used also to provide the necessary "slip" for playing cards. An air-drying lacquer used for this purpose is based on cellulose nitrate or acetate, and plasticisers selected from tricresyl phosphate, triacetin, camphor, Palatinol, Sipalin, castor or linseed oils. Slip is conferred by the addition of montan, carnauba or japan waxes.[25]

In Waterproofing Compositions.—It is not surprising that the natural water repellant properties of waxes have prompted their use in many types of water resisting and water repelling compositions. As Steinle points out, waxes form the natural protective coatings on the skin and hair of animals, as well as on leaves, fruit and blossoms. Their use by mankind dates back to the early days of history.[26]

Solutions of waxes in solvents are used for the impregnation of walls to prevent ingress of moisture, and for paper and textiles. Waxes figure also in lacquer compositions for paper, cellulosic films, etc.

A composition for waterproof transparent sheets is made by mixing a solution of chlorinated rubber and wax in toluene, with a nitrocellulose lacquer derived from cellulose nitrate, wax, triphenyl phosphate and diethyl phthalate, in ethyl acetate and toluene.[27]

Another waterproofing composition based on nitrocellulose contains alkyd—or modified phenol formaldehyde resin, and carnauba wax.[28]

Using a mixture of ethyl and butyl acetates and toluene as solvent, a waterproof flexible lacquer is made from polyvinyl chloride and/or polyvinyl acetate, plasticised with diamyl or dibutyl phthalate, with some wax. Waxes suggested include paraffin, ozokerite, ceresin, beeswax, candelilla, palm, spermaceti or synthetic waxes.[29]

Cements, Stoppers, Adhesives.—Waxes are frequently used for the production of cements, etc., the composition of which varies according

to the use to which the products are put. Natural and artificial bitumens are other common constituents, and fillers are added if desired.

Because of their good compatibility, chlorinated naphthalenes are very popular, and especially if the product must possess good electrical properties or chemical resistance.

A cement composition for application, either as a solution or in molten form, to broken stitches of clothing, consists of wax, Burgundy pitch and resin.[30]

Wax Stains.—Combined stains and wax polishes suitable for application by brush have been introduced. Their functions are to stain wood, and after evaporation of volatile matter to leave behind a wax residue which, on polishing, yields a smooth waxed finish. Fairly soluble waxes which polish easily, such as beeswax, are used in these composite stains.

Printing Inks.—Waxes are sometimes incorporated in overprinting varnishes where they prevent penetration and modify surface tack. They sometimes constitute the major portion of a printing ink. Thus inks for printing on oxidised aluminium are made from beeswax and chrysoidine (3 per cent), or paraffin wax and chromium oxide (10 per cent).[31]

A composition consisting of phenol formaldehyde resin, tung oil and lanolin is added in small amounts to lithographic inks.[32] Waxes figure prominently in carbon paper coatings.

Crystallising Varnishes.—Because of the ease with which chlorinated naphthalenes crystallise from solutions, crystallising varnishes which rely upon evaporation for effect can be formulated from them.

Fireproofing Compositions.—Chlorinated naphthalene waxes, with other chlorinated compounds such as chlorinated rubber and chlorinated diphenyl, are employed in non-inflammable compositions. These are utilised as fire resistant cable waxes, and in lacquers for conferring fire resistance on inflammable materials like cellulose products and fabrics. The chlorinated waxes have been added to rubber to render it fire resistant.

Preservatives or Pest Resisters.—Chlorinated waxes have pronounced insecticidal and fungicidal properties. They resist attack by the death-watch beetle and the tropical white ant. Absence of offensive smell makes them suitable for impregnation of paper and textiles and for the woodwork of houses. Other agents such as copper and zinc naphthenates may be used with these waxes in solutions with advantage, when smell is unimportant.

Molten wax may be used for impregnation in place of solutions.

Insulating Materials.—Most waxes possess valuable electrical insulating properties. In addition, their water repellant properties make them particularly suitable. They are used for electrical insulation where the maximum working temperature of the plant is comparatively low, and where there is no chance of contact with organic liquids such as transformer oils.

Waxes used for impregnation and other electrical purposes, include paraffin, ozokerite, ceresin and chlorinated naphthalenes. Impregnation

is accomplished by immersion in the liquid wax at ordinary pressure or in a vacuum plant.

Anti-Rust Solutions.—The solutions are applied to all types of iron and steel tools and plant to prevent corrosion during transit or on storage. The protection demanded is of a temporary nature only, and whatever coating is used must be removed readily by solvent action.

Solutions of crude lanolin in petroleum hydrocarbons are commonly used for this purpose. In order that their presence may be easily detected they are coloured blue or red. Lanolin itself has no film strength, and is toughened sometimes by adding rosin.

The coatings are removed when required by scrubbing with paraffin oil or white spirit.

Other waxes are used for rustproofing metals. These may be applied by immersion in the molten wax or by using a special Pahl sprayer.[33] Lanolin has a definite hygroscopicity which is not present with many other waxes. Hence under certain conditions the latter may be preferable.

Paint Media.—Waxes are used in cheap paints, and those based on lanolin are by far the most important. Lanolin blends with all the normal varnish constituents, and oil-free blends with natural copals, rosin and rosin ester are common. Such paints possess several defects, including poor film strength, thermoplasticity, inferior flow and handling difficulties.

Anti-corrosive paints with good adhesion and elasticity are based on chlorinated rubber and lanolin.[34]

A method of preparing wax paints consists in stirring the pigment into a fused mixture of wax and resin, cooling and grinding roughly. The product is then dispersed in turpentine and ground more finely. In an example, 70 parts of zinc oxide are stirred into a mixture of 24 parts of wax and 36 parts of resin.[35]

A weather-resisting paint medium is produced, by adding up to 4–5 per cent of beeswax to a linseed oil-resin mixture, and cooking the whole with up to 5 per cent of activator. The activator comprises ionium residues from radium preparation.[36]

Synthetic Resins.—Waxes have been used in the manufacture of synthetic resins.

Waxes such as beeswax, carnauba, montan and spermaceti are reacted with glycerol in the presence of a catalyst. The reaction products yield resins, on heating with phthalic anhydride. A dark resin, soluble in acetone, toluene, and mixtures of alcohol and hydrocarbon, is obtained from montan wax.[37]

Belt Compositions.—A mixture of rosin (400), bleached montan wax (50), and melted blubber (550), is used for thick chrome leather transmission belts.[38]

Polishes.—A considerable amount of wax is used in the manufacture of polishes of one kind or another, including shoe, furniture and floor polishes. Carnauba, candelilla, beeswax, paraffin, montan, ozokerite,

shellac waxes, and the synthetic I.G. waxes are the types most favoured. The polishes are dispersions of wax in hydrocarbons or in emulsions.

The reader is referred to other literature for detailed information on these products.

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CONSTANTS OF WAXES

Natural

Wax.	M.Pt. (°C.).	S.G.	A.V.	S.V.	I.V.	% Ash.
Carnauba	84	0·998	2·5	80	13 [1]	0·05 + [2]
Candelilla	68–70	0·94–0·99	10–20	46–63	— [1]	0·2–0·4 [2]
Ouricoury		1·02–1·03				1·2–1·5 [2]
Ouropardo		1·23				0·7–1·0 [2]
Raphia	79–82					
Sugar cane	82					
Esparto	69–74		30	75		
Shellac	70–84					
Flax	61	0·908	54·5	101·5	9·6	
Cottonseed	86					
Balanophore	up to 100					
Lanolin	35	0·945	5	96–102	25–33	[1] and others
Peat	70–100					
Beeswax	63	0·965	20	95	9	[1]
Portuguese—						
yellow			19	91·5	10·5–11	[3]
white			19·5	92·5	6	[3]
African yellow			19·5	92·5	12–12·5	[3]
Canadian	63·7–64·7	0·962–0·967	16·5–19·6	87–92	7·6–12·4	[4]
Taraxacum root (Japanese dandelion)			17·8	114·9	25·8	[5]
Spermaceti	49	0·960		122–130	3·5–4·0	[1]
Insect	81	0·970		92	1·5	[1]
Gondang	55–73	1·011				
Montan wax—						
(crude)	80–82	1·0	25	58		[1]
(refined)	72–77 / 76	1·0	73–85 / 89–99	91–104		
Ozokerites—						
Russian (crude)	64–84	0·910–0·960				[2]
(refined)	69–88	0·900–0·950				[2]
Polish (crude)	68–90	0·910–0·960				[2]
(refined)	70–90	0·900–0·950				[2]
Rumanian (crude)	88·6					[2]
Petroleum ceresins						
American—						
(crude)	59–71	0·910–0·935				[2]
(refined)	60–73	0·905–0·930				[2]
(Superla, Stanolind)	74–85	0·930–0·940				[2]
Paraffin waxes—						
(ordinary)	40–62	0·870–0·920				[2]
(Asian)	58–75	0·905–0·935				[2]

[1] Fryer and Weston. [2] Ivanovzsky. [3] Lepierre and de Carvalho.
[4] Baril and Lemay. [5] Inoue.

CONSTANTS OF WAXES

Synthetic

Wax.	M.Pt. (°C.).	S.G.	A.V.	S.V.	I.V.	% Ash.
Chlorinated Naphthalenes						
Seekay—						
A68, R68 .	68–72	*				1
A93, R93, R93C	90–95	1·55				1
A700, R700 .	90 approx.					1
A113, R113, R113C .	110–115					1
A123, R123, R123C .	120–125					1
AX111 . .	108–113					1
RX118 . .	117–122					1
Chlorinated Paraffins—						
Chlorowax	90–100	1·6–1·65	—	—	—	5
Lanette wax SX	50–52		< 0·1		< 5	2
Adheso wax .	98–99					3
Ceraflux (Tech.)	53					3
Gelowax A .	*83*					3
Glyco wax A .	58–59					3
Glyco wax B .	54–55					3
Wax B 430 .	81–83					3
Wax No. 181 .	40·7					3
I.G. waxes—						
O . .	105–107·5	1·03–1·04	10–15	123–138		4
OP . .	105–107·5	1·03–1·04	10–15	123–138		3·2–3·5[4]
E . . .	80–83	1·01–1·02	15–20	155–175		4
S . . .	82–84	1·01–1·02	142–152	165–180		4
CR . .	80–83	1·00–1·01	30–35	115–130		4
B (unbleached)	75–77	0·95	10–20	145–165		4
B (bleached) .	75–77	0·96	55–75	165–185		4
N new . .	75·6–77	0·97	35–45	110–125		4
V . . .	50–51·7	0·93–0·94	0	0–10		4
Z . . .	100–103	0·92–0·93	0	0		4

[1] I.C.I. Ltd. [2] Ronsheim and Moore. [3] Rex, Campbell & Co. Ltd.
[4] I.G. [5] Diamond Alkali Co.

* S.G. Trichloronaphthalene is 1·2 approx. S.G. Hexachloronaphthalene is 1·8 approx.

CHAPTER 14

RUBBER

RUBBER, as such, or in its many modified forms, is finding increasing application in products for special purposes.

Source

Rubber, or latex, is derived from the exudation of certain tropical trees and shrubs after incisions in the bark have been made. Species yielding rubber occur in Malaya, the Dutch East Indies, Ceylon, Africa, Siam, Southern India, Burma, Cochin China, and South and Central America. South American rubber, collected in the Amazon district, is shipped through Para, and hence is known as para rubber. All but a few per cent of raw rubber is now obtained from plantations in Malaya and the Dutch East Indies.

Collection and Treatment

When the trees are tapped a milky juice flows away. This is known as latex. It is quite distinct from sap, and should not be confused with it. The latex is collected in small cups. It is a complex dispersion, and the rubber globules in it are made to coalesce by a process known as coagulation. They are then easily removed. Several methods of coagulation are used. The native smoking process consists in allowing a thin stream of latex to flow on to a wooden paddle, which is rotated in the dense hot smoke arising from the burning of resinous woods. Coagulation occurs through rapid evaporation of volatile matter in the latex, assisted by the effect of the organic acids present in the smoke. Or on the plantation coagulation is normally effected by the deliberate addition of acids or acidic substances such as acetic, formic, lactic, sulphuric and sulphurous acids, or sodium hydrogen sulphate and alum. Organic liquids such as alcohol, acetone and formalin also cause coagulation. A method used in Malaya is known as autocoagulation, and involves the addition of a fractional percentage of glucose to the latex. Coagulation takes place in about eighteen hours. Autocoagulation is, however, not popular, and is really of academic interest only.

The coagulated mass is known as Coagulum. In the factories on the plantations this is sliced, macerated between rolls, and washed with water to remove extraneous matter such as dirt, bark, twigs, etc. The rubber is converted into sheets by passage through the rolls, and dried. The product known as crêpe rubber is obtained by drying in the air. When drying is effected in smoke, smoked sheet is obtained. Both crêpe rubber and smoked sheet are known as raw rubber.

Raw rubber is vulcanised by mixing about 6 lb. of sulphur intimately

with 100 lb. of rubber, passing the mixture repeatedly through rolls, and subjecting it to a temperature of 140°–150° C. for several hours. Most of the sulphur in vulcanised rubber is in true chemical combination, although some remains in the free state. An alternative method of vulcanisation, known as the cold vulcanising or curing process, is to steep the rubber in a solution of sulphur monochloride in benzene or carbon disulphide, or to leave it in contact with sulphur monochloride vapour. Peachey uses the combined effect of sulphur dioxide and hydrogen sulphide, on thin sheets of rubber to bring about vulcanisation.[1] Heat vulcanisation is expedited by the presence of accelerators, a short list of which would include the oxides of lead, calcium and magnesium, basic lead carbonate, calcium hydroxide, magnesium carbonate, antimony sulphides and organic bases such as aniline, piperidine, aldehyde ammonia and diamines. Organic accelerators have now almost exclusively replaced inorganic ones, and the principal organic accelerators used are mercaptobenzthiazole, guanidines, and thiocarbamic acid derivatives.

Reclaimed rubber is obtained from old or scrap rubber by heating for several hours with or without alkali, oil, or other materials. Vulcanised rubber scrap is converted to a satisfactory paint medium constituent, by treating it first with carbon disulphide at 60° F. for one hour. Sulphur and carbon disulphide are removed by heating in a hot water bath, the rubber settling to the bottom. After further treatment with caustic soda for two to four hours at 100° C., the rubber is claimed to be free of oxidising agents and fillers. It is ultimately dissolved in benzene, filtered, and the filtrate is used as a paint medium.[2]

Rubber is also oxidised, hydrogenated, acetylated, halogenated, hypochlorinated, nitrited and isomerised. It is in some of these forms that it is used chiefly in varnish and lacquer manufacture.

Chemical Constitution

Rubber is generally considered to comprise a number of C_5H_8 units, often written as $(C_5H_8)n$. A similarity exists between rubber and isoprene which also possesses the formula C_5H_8. Rubber can be synthesised from isoprene, and rubber can be degraded into isoprene. Each C_5H_8 unit of rubber possesses an unsaturated bond which permits the formation of many types of addition compound. Rubber is said to consist of a long chain of C_5H_8 units, and Pickles believes that at least eight are involved in each chain.[3]

Latex

Properties.—Its composition varies considerably, according to the botanical source of the latex, age of plant, season and position of tappings.[4] The rubber is present as an aqueous dispersion. Mineral salts, acids, resins, sugars, glucosides, proteins and enzymes are present also. Below are given three typical analyses of latices.

	1.[4] (Amazon.)	2.[4] (Ceylon.)	3.[5]
Rubber	32·0	41·3	32·0
Albuminoid and mineral matter .	21·0	5·0	12·0
Water	47·0	55·2	56·0

Latices may be either acidic or alkaline. Latex on storage, unless preserved with alkali, gradually becomes acidic and spontaneously coagulates. The addition of sodium bisulphite or ammonia to latex prevents darkening on exposure to air. The latter is often added as soon as the latex is collected.

The effect of bentonite on latex has been studied by Van Rossen. Bentonite increases the viscosity and reduces tackiness. The normal process of coagulation by acids is upset by the presence of bentonite, and flocculation only occurs.[6]

Uses.—Latex is used for a wide variety of purposes. It is best applied by brush or spraying, although electrodeposition on metals has been successfully accomplished. In this respect adhesion is best on zinc. Metals thus coated can be used with acids and for heat, sound and electrical insulation.[7]

A waterproofing composition for jute and textiles contains latex, drying oil, alkalised casein glue, and water. Special processes have been developed for coagulating aqueous latex colloids on fabrics with minimum penetration. A latex composition for impregnation of textiles and paper is based on rubber, 17 parts; silica gel, 0·8 parts; and tannic acid, 0·7 parts. The latter ingredient acts as a stabiliser. A binder claimed to be both water and oil proof contains latex (68 per cent solids), 214 parts, concentrated ammonia, 88 parts, zinc chloride, 5·7 parts, stearic acid 24 parts, borax 18 parts and casein 100 parts.[8]

A fire and waterproof coating for electric cables and wires is made by mixing a dispersion of a halogenated benzene or halogenated phenanthrene derivative in a non-solvent, with a rubber dispersion.[9]

The alkali resistance of rubber is made use of in a medium for plaster paints which is an emulsion of rubber latex and waxes.[10] Other paint media are derived by adding a solution of an alkali silicate to a mixture of gelatinous silica and latex, or by mixing casein, water, concentrated ammonia and latex.[11] Mixtures of this type sometimes form the basis of distempers, and part of the casein may be substituted by glue with advantage. A distemper for plaster walls contains latex with ammonia, and protective colloids such as soap or glue. Substances like the fluosilicates of aluminium, magnesium and zinc, or sodium silicate are incorporated also. Their object is to react with the plaster to give good adhesion.[12] A road-marking paint, in which the pigment is either lithopone or chrome yellow, is made from a stabilised mixture of latex and calcium or sodium caseinate. Drying oils are incorporated also, if desired.[13] The

presence of a stabiliser such as alkalised casein is necessary, when pigments are ground into latex, in order to prevent the breakdown of the emulsion. Pigmented water paints on latex are not entirely satisfactory, even with a stabiliser present, for the latex tends to coagulate and clog the brush.

Wheat, corn, rice, tapioca, potato or arrowroot starches are added to latex, together with stabilisers. The resultant composition is used for coating the backs of carpets and rugs. It may be vulcanised.[14]

Another interesting application is in compositions for lining ends of cans. A typical formula is alumina, ammonium alginate, saponified wax and latex. A similar sealer for containers is a mixture of latex six parts and alginic acid four parts.[15]

Greaseproof paper is made by impregnation with a composition obtained by adding an alkaline aqueous solution of casein containing formaldehyde to rubber latex.[16]

A priming varnish for leather over which cellulose is applied consists of a mixture of latex, oleoresinous varnish, ammoniacal casein solution and formaldehyde.[17]

The poor adhesion of latex enables protective coatings to be formulated which are easily removed. A latex mixture containing castor oil, casein and kaolin is used as an easily removable protective coating. It is coagulated by spraying on acidic substances such as dilute formic or acetic acid.[18]

A wood filler comprises rubber latex, cellulose acetate, drying oil, sodium salicylate, water and filler.[19]

A composition resistant to hydrocarbons and mineral oils, which is used for gaskets, wire coatings and oilproof cloth, consists of a blend of latex with an alkyd dispersion. Vulcanising agents may be added also.[20]

Raw Rubber, Caoutchouc and Crêpe Rubber

Properties.—Rubber is a plastic substance, but plasticity varies considerably with temperature. Films of rubber show marked solvent retention and tend to remain tacky. They lack both toughness and adhesion.

Rubber dissolves slowly in petroleum, aromatic and chlorinated hydrocarbons, to yield solutions of exceptionally high viscosity. The large quantities of thinner necessary to yield solutions of workable viscosity, result in very thin films which have little protective value. Thus considerable work has been conducted with the object of reducing the viscosity of solutions. Stevens and Heaton [21] found that the most satisfactory solutions were obtained using milled rubber in white spirit in the presence of certain metallic soaps. The table below shows the results obtained with some of the many catalysts tried.

Solution.	Viscosity after 2 days (in secs.).
12½ per cent milled rubber soln.	35
+ 0·5 % lead linoleate	8
+ 0·5 % litharge	18
+ 0·5 % lead acetate	34
+ 0·5 % trichloracetic acid	15
+ 0·5 % benzoyl peroxide	23
+ 0·5 % dinitrobenzene	31
+ 0·5 % iodine	34

The effectiveness of soluble metallic soaps is emphasised in the results given below. Their addition causes an immediate substantial reduction in viscosity, and ageing results in further reductions.

Solution.	Viscosity (centipoises) at 25° C. after—	
	1 day.	1 month.
10 % milled crêpe rubber in white spirit	7040	6080
+ 1 % cobalt linoleate	540	125
+ 1 % manganese linoleate	1210	174
+ 1 % copper linoleate	1560	366
+ 1 % lead linoleate	1865	1400
+ 1 % zinc linoleate	2700	1430
+ 1 % iron linoleate	3260	1730

These workers concluded that when using cobalt linoleate, 2·5 per cent, or when using lead linoleate, 10 per cent, on the rubber are satisfactory proportions. The corresponding metallic oleates, resinates, tungates and naphthenates may be used.

Using resinates which were added to a 1 per cent solution of crêpe rubber in benzene, Krauz and Franta found the following order of activity which varies somewhat from that obtained by Stevens and Heaton, cobalt, manganese, iron, lead, copper and zinc. Depolymerisation and disintegration increased with cobalt concentration, and turbidity or sedimentation occurred. When large additions of cobalt resinate were made the speed of depolymerisation was so great that simultaneous oxidation was limited.[22] The catalysts may be added either in the form of a solution to the rubber solution, or incorporated in the rubber during the milling. During mastication of the rubber, the rollers are kept warm. Cobalt, manganese and copper are said to have a detrimental effect on the mechanical properties of the rubber.[23]

Antioxidants like pyrogallol, oxyhydroquinone, α and β-naphthol, *p* and *o*-amino phenol, α and β-naphthylamine, and diphenylamine, inhibit the action of cobalt on rubber. The presence of a keto group in the

molecule was found to nullify the effect of an hydroxyl group. Meta compounds are inactive.[22]

It has been recorded already that cobalt linoleate and similar catalysts cause a progressive depolymerisation of rubber during storage. This excessive and continued viscosity reduction may be a disadvantage. Addition of antioxidants, e.g. hydroquinone, are effective in inhibiting further viscosity reductions. If rubber solutions of reduced viscosity, due to presence of catalyst, are stored as concentrated solutions, there is less chance of further loss of viscosity, such as is exhibited by solutions which are initially thin.

Liquid products are produced from rubber, balata or gutta-percha, by a process of mechanical working involving treatment in an internal mixer. Petroleum or aromatic hydrocarbons are then added, and the mixture passed through a high speed colloid mill until the desired viscosity reduction is attained.[24]

The viscosity of rubber is reduced by other means such as oxidation, chlorination, and isomerisation, or by treatment with tin tetrachloride.[25]

Raw rubber generally, in its untreated form, has poor compatibility with oils and other varnish ingredients. After treatment for reduction of viscosity, its compatibility is improved, and mixtures may be made with drying oils such as linseed oil, tung oil, and stand oils, and with ester gum and other resins, both natural and synthetic.

Raw rubber has good chemical and water resistance, as well as satisfactory electrical properties. It has been used to increase the dielectric strength of drying oils.[24]

Rubber solutions are very prone to cobwebbing. A composition claimed to be sprayable is made by adding an emulsifying agent or protective colloid to a dilute solution of rubber in benzene. An example contains rubber 55, sulphur 3, accelerator 1·5, zinc oxide 35, oil 5·5, and solvent.[26]

The adhesion of rubber is improved by admixture with oil.

Molten Rubber

When raw rubber is heated up to 300° C. liquefaction and darkening occur. Molten rubber possesses drying properties when driers are present. Durability is not good, since the exposed film has a marked tendency to develop cracks. More durable products are obtained if linseed oil is added to the molten rubber. A solution of molten rubber in white spirit containing cobalt drier has been used as a paint medium. Heat liquefied rubber is also used in printing inks.[27]

Uses.—The incorporation of rubber into varnishes and paint, enamel, and distemper media, produces valuable results. It confers on highly pigmented flat paints good flow such that brushmarks disappear, as well as a substantially reduced settling tendency. It has been found to be effective with a wide range of pigments and fillers.

A flat paint, using a mixture of equal parts of oil and rubber as the

medium, flows perfectly when brushed, thus obviating the necessity of stippling. Rubber also enables large surfaces to be coated, without encountering difficulties in joining up. Additions of raw rubber to paint cause livering, which is not the case if a rubber solution of reduced viscosity is used. Oil paint media containing rubber have enhanced wetting properties. The presence of rubber in a pigmented product appears to have no detrimental effect on durability. In flat paints, Stevens and Heaton suggest using up to 50 per cent of rubber calculated on the non-volatile medium, and between 15–30 per cent in exterior paints.[50]

Rubber, linseed and tung oils, kauri, ester gum, manganese borate, zinc sulphate, and red lead, dispersed in a mixed solvent consisting of solvent naphtha, petroleum and turpentine, provides a satisfactory paint medium.[28] A vulcanisable rubber paint is made by adding an oil or varnish paint medium and piperidine and cyclohexylamine in benzene, to a mixture of raw rubber, zinc white, sulphur, iron oxide, powdered asbestos, chalk, lampblack, turpentine and benzene.[29]

In gloss paints and enamels the addition of rubber gives an improvement in gloss. A white distemper can be made from an emulsion derived from a crêpe rubber solution in white spirit containing a metallic soap catalyst, and an aqueous glue solution pigmented with lithopone. Another distemper can be made by mixing a solution of crêpe rubber in white spirit containing 2·5 per cent cobalt linoleate, water, casein and lithopone, with either mineral spindle oil, or with whiting and mineral lubricating oil. Casein may be replaced by gelatin or glue if desired, and its solution is effected by means of ammonia, borax or an alkylamine.[30]

The following methods may be used to incorporate rubber in oils and oleoresinous compositions. Milled rubber is dissolved in solvent preferably with cobalt linoleate and the solution added to the oil or paint. The mixture of rubber solution and oil can be used as a grinding medium.

Raw rubber may be dispersed in drying oils with driers by heating in the usual way. The product can be thinned with white spirit as desired. Tung oil, boiled linseed oil, rosin, rubber and a metallic soap are heated at 300° F. until the mixture is homogeneous.[31]

Another process consists in heating a mixture of drying oil, such as tung oil or boiled linseed oil and rosin to 300° F. Cobalt linoleate is added and the temperature raised to 540° F. Then the rubber is introduced and the heating continued at 600°–650° F. until it dissolves.[32]

A product suitable for use as a paint is derived by heating together powdered Trinidad asphalt and rubber, with or without mineral oil, linseed oil or rosin.[33]

Solutions of rubber in suitable solvents are sprayed on metals to prevent corrosion. A composition comprising rubber, rosin, and tung oil stand oil gives good results in protecting steel panels against the corrosive action of sea-water.[34] A temporary lacquer to prevent rusting relies substantially upon rubber.

Rubber solutions are used as undercoats for cellulose. A primer for

wood, suitable for the subsequent application of a nitrocellulose lacquer, contains a blend of three parts of rubber to one part of nitrocellulose in a suitable solvent.[35] Viscose solution is used in another varnish. Other ingredients include rubber solution, rosin, camphor, drier, turpentine and benzene.[36]

A complex mixture of raw rubber, tung oil, linseed oil, varnish, japan drier, creosote, turpentine, white lead and lampblack is used as a top dressing for cars.[37]

A vulcanisable rubber composition containing sulphur, plasticiser and lampblack is applied to walls and vulcanised *in situ*. A coating resistant to chlorine water is obtained.[38] An acid resisting paint is formulated on thermoplastic rubber dissolved in solvent, and contains ebonite dust. Thermoplastic rubber is made from rubber by the action of phenol sulphonic acid.[39]

The use of rubber occurs in many waterproofing compositions. An example consists of a metallic salt of a higher fatty acid and a solution of rubber, with a vulcanising agent and an accelerator. The metallic salt is present in a preponderating amount.[40]

A medium suitable for pigmentation, for coating the interiors of sponge rubber moulds, is a solution of raw rubber, rosin, stearic acid, sulphur, zinc oxide and mercaptobenzothiazole in benzene.[41]

A mixture of rubber solution, partly polymerised mono or divinyl acetylene, vulcanising agent and drier, is used as a cement for india-rubber. An adhesive insoluble in water consists of natural resin 1–2 parts, unvulcanised rubber 2–1 parts, and plasticiser or an antioxidant, chosen from β-naphthol, aldol-α-naphthylamine, phenyl-β-naphthylamine, or sym. di-β-naphthyl-*p*-phenylenediamine. The solvent may be benzene. The adhesive may be applied to tape which is used as a cap seal for containers.[42]

A priming coat for metal foil, suitable for the subsequent application of adhesive, comprises reclaimed rubber, balata, resinous pitch and zinc oxide.[43]

Vulcanised Rubber

Properties.—Vulcanised rubber is not much used in the varnish trade. Although vulcanisation removes many of the defects and enhances many of the valuable properties of raw rubber, it results in reduced solubility and compatibility. It is for this reason that it has not found widespread application. Vulcanised rubber is less susceptible to temperature changes than raw rubber, which develops stickiness at high temperatures and becomes brittle at low temperatures. Vulcanisation improves stability to temperature variations, tensile strength and chemical resistance, and gives elasticity. Surface tack is eliminated.

Uses.—Six parts of vulcanised rubber and one part of mineral, vegetable or fish oil are macerated together for several hours at 300°–600° F. Finally, a homogeneous fluid results which, after thinning, yields films

capable of oxidation. The solution is pigmented to give a paint.[44] Another paint medium consists chiefly of a blend of vulcanised oil and vulcanised rubber. It is prepared by heating stearin-free fish oil and sulphur under pressure. The product is dissolved by heating under pressure in a solvent chosen from benzine, benzene, turpentine, tetrahydronaphthalene and trichlorethylene. Rubber and more sulphur are then added and the whole mixture is vulcanised under pressure. When vulcanisation is complete the product is thinned with hydrocarbons. Oils and waxes may be added if desired.[45]

Oxidised Rubber

Manufacture.—Oxidised rubber is a valuable varnish and lacquer ingredient. Rubber has a tendency to oxidise in the air and this is accentuated by mastication over hot rollers. Oxidised rubber is known as Rubbone. Raw rubber is dissolved in benzene, carbon tetrachloride, chloroform, or white spirit, and oxidised by air, oxygen, or ozonised air, at 50°–90° C. in the presence of oxidation catalysts. Suitable catalysts are the oleates, tungates, linoleates and resinates of cobalt, manganese, lead and copper. After the oxidation is concluded some methods involve the removal of the metallic salts. During oxidation the linoleates and tungates are precipitated, and this facilitates removal, which is accomplished by centrifuging, decantation or filtration. The solvent is removed by evaporation to leave a pure oxidised rubber.[46]

In a typical example a solution of milled rubber is made in white spirit (20 pts. rubber to 100 pts. white spirit). Cobalt linoleate (15 pts.) is added, the temperature raised to 80°–90° C. and air bubbled through for approximately six hours. A flocculent precipitate, probably oxidised cobalt linoleate, is removed and the solvent evaporated.

A natural dispersion of rubber (latex) is oxidised by air or hydrogen peroxide in the presence of metallic salts. In addition to the catalysts already mentioned, zinc linoleate, zinc oleate, copper acetate and copper sulphate may be used.[47]

Another method implies that the viscosity of the rubber solution is first reduced by the action of metallic salts and then oxidised subsequently by means of oxygen or ozone.[48]

Properties.—Rubbones are available with varying degrees of oxidation. The extent of oxidation varies from one oxygen atom for four isoprene units to one oxygen atom for each isoprene unit.

The effect of oxidation is to reduce the viscosity of solutions in many solvents. Solutions of reasonable viscosity are obtained with petroleum hydrocarbons, and aromatic hydrocarbons yield lower viscosities still. As the extent of oxidation increases, the solubility in acetone and ethyl alcohol increases also. This applies also to butyl Cellosolve and glycollate, Cellosolve, diacetone alcohol, dioxan, isopropyl alcohol, methyl Cellosolve and methyl ethyl ketone. With some solvents, however, increase in extent of oxidation results in reduced solubility. Such solvents are:

carbon disulphide, Decalin, white spirit and turpentine. Among good solvents for oxidised rubber in various states of oxidation are: amyl, butyl, cyclohexyl, ethyl and methyl acetates; benzene, toluene and xylene; butyl alcohol, carbon tetrachloride, methylene and ethylene chlorides, cyclohexanone, and methyl cyclohexanone, dipentene, Tetralin, and mineral oils. Methyl alcohol is a non-solvent.

Compatibility with plasticisers is good, especially with tributyl, tricresyl and triphenyl phosphates; cyclohexyl, diamyl and sextol phthalates; ethyl, butyl and amyl citrates, Barkite B, castor oil, blown castor oil, linseed oil, chlorinated diphenyl, chlorinated paraffin waxes, cyclohexyl and methyl cyclohexyl oxalates, and T oil. Rubbone is incompatible with dimethyl glycol phthalate, Glyacol and triacetin.

Compatibility with other varnish ingredients is good. It blends readily with pure and modified phenolic resins, maleic resins, coumarone, urea formaldehyde, most alkyds and chlorinated rubber. Incompatibility occurs with vinyl acetate resins and some alkyds and acrylic resins.

Oxidised rubber has good chemical resistance, although the alkali resistance is somewhat inferior to that of the unoxidised rubber, as evidenced by a saponification value of 60 approx.

It polymerises on heating to yield insoluble gels, some oxidation occurring simultaneously.

The duration of heating necessary to effect complete polymerisation varies considerably with the temperature. At 300° C. only a few seconds exposure are necessary, but at 100° C. the time required is of the order of two days. Hardening may be accelerated by the addition of certain agents such as potassium permanganate, ammonia and oxalic acid, the two latter being particularly effective.

Water resistance is excellent and electrical properties are good, especially when cooked with stand oil. Odour and taste are slight. Heat resistance is outstanding.

Oxidised rubbers may be vulcanised, but for this purpose the least oxidised products are the most satisfactory.

Rubbones are readily emulsified.

Uses.—Rubbones are used in many oleoresinous varnishes and media, in which they may be regarded as substitutes for natural and synthetic resins. No elaborate treatment is necessary to obtain satisfactory mixtures. A simple solution in white spirit may be added directly to linseed or tung oil stand oils, or Rubbone may be heated at 260° C. with linseed stand oil for about one hour and then thinned. Cooked varnishes are generally superior to cold cut varnishes. The procedure with tung oil is similar, but the addition of a small percentage of pure phenolic resin is advantageous in order to minimise any webbing tendency.

The above oil-Rubbone mixtures can be pigmented as required.

Rubbone, in conjunction with tung oil, figures prominently in chemical resistant finishes, which are claimed to withstand the following reagents:—concentrated acetic and hydrochloric acids, 50 per cent sulphuric, 15 per

CONSTANTS OF OXIDISED RUBBERS

Reference.	Remarks.	Acid Value.	Solubility.	S.G.	Recommended Uses.
RUBBONE A.	Oxidised rubber (1 atom of oxygen 4 isoprene units)		C.S. white spirit and aromatic hydrocarbons I.S. acetone and alcohol		For vulcanisation.
RUBBONE B	Oxidised rubber (1 atom of oxygen 2 isoprene units)	5	C.S. white spirit, aromatic hydrocarbons, acetone and drying oils I.S. alcohol	0·966	Chemically resistant varnishes. Flexible and heat resistant. Insulating varnishes, wire enamels and tin coating lacquers. Oil in water emulsions.
RUBBONE C	Oxidised rubber (1 atom of oxygen 1 isoprene unit)		C.S. alcohol, acetone, aromatic hydrocarbons I.S. white spirit		Alcoholic lacquers containing shellac, Manila, etc.
RUBBONE SH	Oxidised rubber (high viscosity)		C.S. acetone, aromatic hydrocarbons I.S. alcohol, white spirit		For application to wood as sealers, and to concrete as primers. Oil in water emulsions.
RUBBONE SL	Oxidised rubber (low viscosity)		As SH above		

cent nitric, organic acids, 20 per cent caustic soda, salt and sugar solutions, and plating solutions. Good resistance to chemical reagents is maintained even at elevated temperatures. A paint medium made from Rubbone, phenolic resin, and tung oil is claimed to be resistant to methyl salicylate or mustard gas after air drying for seven days. These types of varnish are also resistant to alcohol and hot mineral oils.

The excellent water and acid resistance of Rubbone-oil stoved films, coupled with good flexibility, has suggested their value as gold stoving varnishes for food containers. Rubbone-tung oil mixtures are used as spar varnishes.

The heat resistance of Rubbone makes it a useful ingredient of heat resisting finishes for radiators, exhaust pipes, etc., and blends with linseed oil are claimed to withstand temperatures of the order of 200° C.

Insulating compositions for the impregnation of paper, textiles, asbestos and coils are based on Rubbones. The impregnation of coils in liquefied Rubbone at 100° C. has been suggested. If the oxidised rubber is cooked into oils a product with enhanced insulating properties is obtained. Oxidised rubber is especially recommended in compositions for use on electrical apparatus which functions under highly humid conditions. Lacquers for wire enamels are stoved at high temperatures. Mixtures of oxid sed rubber, linseed oil, and bitumen, give satisfactory results under these conditions of application on tinned copper wire. Inhibition of dry occurs on copper wire and the above composition should not be used on it.

Anti-corrosive primers, undercoatings and finishing paints for iron and steel are based on tung oil and Rubbone.

A high coefficient of friction with excellent heat resistance makes Rubbone a useful binding medium for brake linings. It is also useful as the adhesive for the abrasive of disc grinders.

Introduction in printing inks improves gloss and dry, and prevents penetration. If large percentages of Rubbone are used it can function as a matting agent.

Its low acidity makes it a useful component of aluminium media.

A paste filler for metal requiring stoving is made by heating Rubbone, sulphur, zinc oxide and silica at 150° C. for one hour. The resultant product is thinned with benzol as desired.

Isomerised Rubber

An isomerised rubber has been offered under the description, Resin 500R. It differs from rubber in that it is believed to have a ring formation, and this may provide the explanation for the reduction in unsaturation. Isomerised rubber is less susceptible to oxidation than raw rubber.

Solubility is good in aliphatic, aromatic and chlorinated hydrocarbons, and it is compatible with oils and many plasticisers, as well as natural and synthetic resins, including the phenolic and alkyd types. Solutions suitable for spraying without cobwebbing can be made in white spirit.

Adhesion is good, but flexibility is inferior to that of normal rubber, the isomerised rubber being brittle. The melting-point of isomerised rubber varies from 50°–130° C.

The saponification value is low, and resistance to alkali and acid is good. It is especially recommended for resistance to glacial acetic acid.

On heating, films fuse at first, but subsequently become tougher. Heat resistance is good, no substantial deterioration being observed at temperatures up to 200° C.

A varnish can be made by heating a rubber isomer with linseed stand oil and tung oil for about an hour. After lead and cobalt naphthenates are added, the product is thinned with white spirit.[49]

Hydrogenated Rubber

Because of its unsaturation rubber may be hydrogenated. This is accomplished in the presence of a solvent, such as white spirit, and a catalyst. Thus products which are used as varnishes or media are prepared by heating equal parts of rubber and petroleum distillate (b.pt. 130°–200° C.) in an autoclave for three to six hours at 200°–300° C. and 50–150 atmospheres pressure, with hydrogen, using a nickel catalyst. Hardness is obtained by the addition of other resins.[51]

A coating for fabric is made from hydrogenated rubber, alkyd resin and ethyl cellulose.[52]

Peracetylated Rubber

This is prepared by treating a solution of raw rubber in chloroform with glacial acetic acid and hydrogen peroxide at temperatures in excess of 60° C. The product blends satisfactorily with nitrocellulose, and natural resins like damar and plasticisers may be added.[53]

Rubber Resins

Many modifications of rubber are classified as rubber resins.

A homogeneous mass is made by kneading together vulcanised rubber and coumarone or indene resin at 120°–130° C. Rosin can partly replace the vulcanised rubber. A rubber-coumarone resin is obtained by dissolving rubber in a solvent containing the polymerisable constituents of coumarone or indene resins and effecting polymerisation by means of sulphuric acid.[54]

A phenolised rubber resin is obtained by heating an oil soluble heat hardenable phenolic resin with rubber in two stages. The preliminary heating is conducted at a low temperature, and after kneading the process is continued at a higher temperature.[55]

A rosin-rubber resin, based on 3·4 parts of rosin to one part of rubber, involves heating the rosin to 300° F., adding 2–4 per cent of cobalt linoleate calculated on the rosin, and raising the temperature to 540° F. The

rubber is then added and the heating and stirring continued until homogeneity is attained. Fused rubber rosinates are esterified with glycerol at temperatures above 460° F.[56]

Pliolite Resin

This resin is an amber coloured thermoplastic compound containing at least 92 per cent of rubber. A modification containing one part of ester gum to two parts of rubber resin is available also.

Pliolite is an oxidisable resin, oxidation being facilitated by addition of driers, by stoving, or by the action of light. Up to 8 per cent of oxygen is absorbed. The oxides of titanium, chromium and iron act as hardening agents, but hydroquinone, pyrogallol, phenyl-β-naphthylamine, and zinc oxide, inhibit oxidation.

Pliolite is soluble in petroleum hydrocarbons but insoluble in alcohol and acetone. Compatibility with drying oils such as linseed, tung and fish oils is satisfactory, and the usual plasticisers such as butyl phthalate and stearate, tricresyl phosphate, and chlorinated diphenyl are suitable if desired.

Its outstanding properties include absence of taste and odour, good acid, alkali, water and abrasion resistance, and excellent flexibility, adhesion and electrical properties.

Synthetic Rubber

Certain products obtained by direct chemical synthesis are described as synthetic rubber. A typical example is the olefine polysulphide compound, derived by the interaction of ethylene dichloride and a soluble polysulphide such as sodium tetrasulphide. The synthetic rubber produced has an empirical formula of $C_2H_4S_4$.

Thiokols A and F are representative examples of this type of compound.

Thiokol is similar to heavy pale crêpe rubber and needs compounding and vulcanising. Special processing is suggested. A compound suitable for vulcanising is prepared by first milling the Thiokol over tight warm rollers. Plasticisers such as diphenyl guanidine and tetramethyl thiuram disulphide are then added. Broken down rubber, carbon black, zinc oxide and stearic acid are then added in this order.

Crane gives the following quantities of the individual ingredients :[57] Thiokol A—100, smoked sheet rubber—5, zinc oxide—10, channel black—25, stearic acid—0·5, diphenyl guanidine—0·15, tetramethyl thiuram disulphide—0·20. Zinc oxide is the vulcanising agent and the sheet rubber is present to facilitate handling. A similar mixing for Thiokol F involves the use of mixed plasticisers, benzthiazyl disulphide and diphenyl guanidine.

The compound prepared from Thiokol A cures in fifty to sixty minutes

at 40 lb. steam pressure. The Thiokol F compound cures in a similar time at 50 lb. steam pressure.

Thiokols are most satisfactory for their excellent solvent resistance after curing, and in this respect grade A is superior to grade F. Thiokol A, after one year's immersion in petrol, lubricating oil, fuel oil, turpentine, or carbon tetrachloride shows no swelling. With benzol, 1·5 per cent swelling occurs. After similar immersion, Thiokol F shows 1 per cent swelling in petrol, 0·8 per cent in paraffin, 25 per cent in benzol, 1·3 per cent in raw linseed oil, 2·5 per cent in acetone, 1·3 per cent in methyl alcohol, 8·8 per cent in carbon tetrachloride. Complete destruction occurs with ethylene dichloride. The percentage swelling is calculated by measuring the increase in length of a strip $1\frac{1}{4}$ in. by $\frac{1}{16}$ in. by 4 in. long.

In addition to solvent resistance, Thiokol F resists dilute acids and alkalis, although concentrated sulphuric and nitric acids destroy it. Resistance to ozone is good.

Olefine polysulphides are sensitive to heat above 80° C. They possess high specific gravities covering the range 1·6–1·7.

From the varnish maker's point of view, probably the most important use is in impregnating compositions for fabrics. Thiokol F may be prepared as a solution in ethylene dichloride, or in a mixture of this solvent with benzol. Vulcanisation of the treated fabric is effected by festooning at 125° F.

Other synthetic rubbers are Polythene and Polyisobutylene, but the reader is referred to a comprehensive recent publication for detailed information on these compounds.[58]

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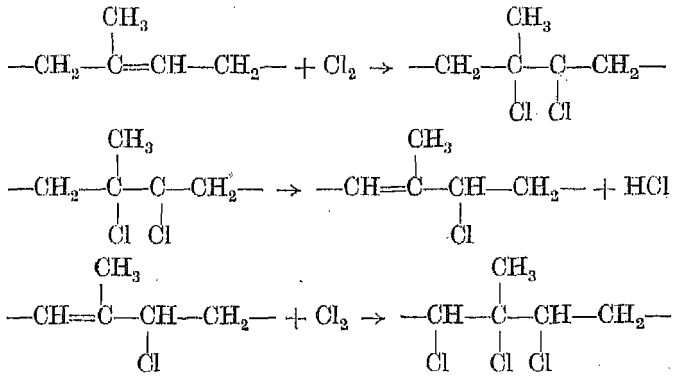
CHAPTER 15

CHLORINATED RUBBER

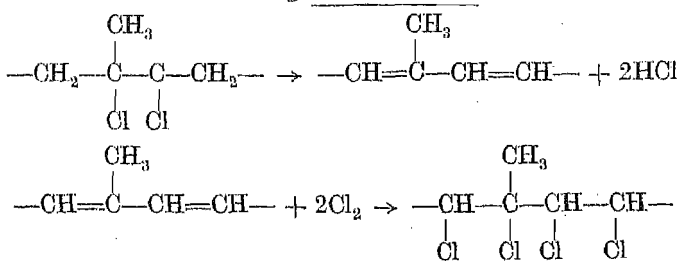
Mechanism of Halogenation

FLUORINE, chlorine, bromine, and iodine all react with rubber. The reaction is not a simple addition to the unsaturated bond. Each isoprene unit (C_5H_8) contains one unsaturated bond, and this should accommodate two chlorine atoms. The resultant product would contain 51 per cent chlorine. In fact, chlorinated rubber contains percentages of chlorine greatly in excess of this figure, and, furthermore, during the halogenation process hydrochloric acid is eliminated. It has been shown experimentally that during halogenation of rubber considerable substitution occurs in the early stages of the process, but that later addition becomes more pronounced.[1]

Kirchof's theory for the reaction is that chlorine adds on to the unsaturated bond initially, yielding a completely saturated product. This then disintegrates, losing either one or two molecules of hydrochloric acid for each isoprene unit, and resulting in the formation of unsaturated compounds again. The unsaturated compounds possess either one or two unsaturated bonds, depending upon whether one or two acid molecules are eliminated. Additions of chlorine then occur at these unsaturated bonds.[2] Heat is generated during chlorination.



Reaction involving loss of one HCl molecule.



Reaction involving loss of two HCl molecules.

Manufacture

Chlorinated rubber may be manufactured by treating rubber in its many forms with chlorine.

From Rubber Solutions.—It may be effected on solutions of rubber in certain solvents. Among the solvents which have been used are carbon disulphide, chloroform, carbon tetrachloride, benzene, or its homologues, chlorobenzene, chloronaphthalene, alkyl and alkylene halides, and petroleum hydrocarbons. It is obvious that the choice of solvent will be controlled by two considerations, firstly, by its solvent power for the rubber modification used, and secondly, by its resistance to attack by the chlorinating agents. Adjustments in process have been introduced to enable solvents to be used which normally would be attacked.[3] Water has also been used as the dispersing medium. Solutions of rubber in organic solvents for chlorination are normally dilute. B.P. 390,025 enumerates the plant necessary for chlorination of rubber, in solution, as follows :—

A vessel in which the solution of rubber is made, a mechanically agitated reaction vessel, recovering plant for evolved gases, and means for evaporation of solvent from the chlorinated rubber solution. A refinement includes an expansion valve for high pressure chlorination.

Crêpe rubber (25 pts.), in carbon tetrachloride (800 pts.), is chlorinated at ordinary temperatures.[4] Another process involves the chlorination of a 10 per cent solution of milled rubber in carbon tetrachloride.[5] During the early part of chlorination the solution becomes opaque, but it clears again subsequently. A 4·2 per cent solution of rubber in carbon tetrachloride has its viscosity reduced by irradiation. Chlorination is effected by passing into this solution at 60°–75°, chlorine saturated with carbon tetrachloride.[6] Exposure of the rubber solution to irradiation, with ultra-violet or infra-red rays, may take place before or during chlorination. In an example, a solution of rubber in carbon tetrachloride is exposed to a mercury vapour lamp, and then chlorinated during continuous exposure for eight hours. After a further twenty-four hours' exposure to the light, a low viscosity chlorinated rubber is obtained.[7]

The viscosity of rubber solution before chlorination may be reduced by mastication of the rubber, or by treatment with metallic salts of which copper oleate is suggested.[8] The high viscosity of a rubber solution in a non-aqueous solvent is reduced, before chlorination, by boiling under reflux.[9]

Rapid halogenation is advocated to improve stability. A stream of rubber solution is introduced slowly into a vessel containing sufficient halogenating agent to promote a speedy reaction and to take the reaction rapidly beyond a critical point.[9] Solutions of rubber and chlorine are reacted together in the presence of water, which abstracts the hydrochloric acid formed. Sodium hypochlorite has been suggested as an oxidising agent which is effective in reconverting the free hydrochloric

acid to chlorine. Hydrogen peroxide and hypochlorous acid are other oxidising agents which have been used in reactions conducted in the presence of water.[10]

From Latex.—Another form of rubber which can be used in the manufacture of chlorinated rubber is latex, the dispersion of rubber in water. Most of the water of a latex is evaporated by heating with a solvent such as chloronaphthalene or chlorobenzene above 100° C., and the resultant solution or suspension is chlorinated.[11]

A vigorously agitated solution of latex is chlorinated by passing chlorine into it until the chlorine content reaches 5–15 per cent. After concentrating the dispersion by filtration it is subjected to a further chlorination at 80° C.[12] The latex may be pretreated before chlorination. One method involves oxidation by means of air, oxygen or hydrogen peroxide, conducted in the presence of catalysts, including cobalt nitrate or linoleate, copper sulphate or oleate, manganese or nickel sulphates, or iron oxide. Halogenation is conducted at 40° C. until the product contains 40–60 per cent chlorine.[13]

Another method stabilises the latex by vulcanisation, or by the addition of glucosides, sodium alkylnaphthalene sulphonates, or compounds derived by sulphonating phenols and hydrocarbons in the presence of aliphatic unsaturated acids. After this preliminary treatment chlorine is passed in.[14] When chlorine is passed into vulcanised latex, precipitation occurs. After separation of the precipitate it may be chlorinated further.[15] An aqueous suspension of finely divided rubber has been used as the starting material and is converted to chlorinated rubber (70 per cent chlorine) in two stages. In the first stage chlorination is allowed to proceed below 40° C. until the resultant product contains 30–40 per cent chlorine. This is ground finely, redispersed in water and treated with more chlorine until the halogen content becomes 70 per cent.[16]

From Solid Rubber.—Solid dry rubber has been chlorinated also. The action is slow but it can be facilitated, according to Ellis, by exposing the rubber to chlorine during mastication.[17] Continuously agitated, finely divided rubber is subjected to the action of chlorine in an enamelled or lead-lined vessel. If a continuous process is used the fine chlorinated rubber powder is removed by the current of chlorine.[18]

The use of a mixture of chlorine and carbon tetrachloride vapour has been suggested, the function of the solvent vapour being to soften the outer layers of the solid rubber to permit easier access for the chlorine.[19] The idea of using a solvent as a softening agent for the rubber is taken a step further in a process which consists of suspending strips of rubber in carbon tetrachloride and chlorinating. Since the chlorinated rubber is very soluble in the carbon tetrachloride it is rapidly dissolved away, leaving fresh soft rubber exposed to the halogenating agent.[20]

Effect of Temperature and Pressure.—Ellis has recorded that halogenation proceeds more readily as the temperature is increased, and that temperatures near the boiling-point of the solvent are especially

favourable.[21] The same worker has indicated the advantages of conducting the reaction under pressure.[22]

Other Chlorination Processes.—Chlorination of rubber may be effected in the presence of agents other than the halogenating reagent. Thus, rubber is chlorinated in solution or as a suspension in the presence of iodine.[23] Additions of naphtha sulphonic acids or their sodium salts are added to rubber in carbon tetrachloride before chlorination, in another protected process. Rubber is heated to 200°–300° C. with a fatty acid soap, dissolved in carbon tetrachloride and chlorinated.[24] Many examples of chlorination in the presence of sulphur have been recorded. A solution of rubber containing sulphur is subjected to the action of chlorine.[25] Ten grams of masticated crêpe rubber are dissolved in 200 c.c. of carbon tetrachloride and one gram of sulphur is added. Treatment with chlorine follows, and finally a product is obtained containing 32 per cent chlorine which is soluble in acetone or benzene.[26] In the earlier stages of chlorination gelation occurs, but further treatment causes re-solution. Some processes stop halogenation at the gelation stage. For example, chlorine is passed into a solution of rubber (10 g. in 320 g. CCl_4) containing 1·5 g. sulphur until a stiff gel is obtained. After washing the product first with carbon tetrachloride and then with boiling water, it is dried. The chlorine content is 20 per cent.[27]

The Separation of Chlorinated Rubber.—After the reaction chlorinated rubber is obtained as a dry product by several methods. The most obvious one is by evaporation of solvent. An agitated solution of chlorinated rubber is treated with steam. Steam and solvent vapour are evacuated simultaneously.[28]

A solution of chlorinated rubber in carbon tetrachloride is fed beneath the surface of water which is maintained above the boiling-point of carbon tetrachloride and kept vigorously stirred. The rubber solvent is evaporated, and the chlorinated rubber generated in a porous, spongy or fibrous condition at the surface of the water. Alternatively, the solution is flowed on to the surface of hot water which is kept moving.[29]

Chlorinated rubber is precipitated from solution by the addition of a non-solvent such as methyl alcohol or mineral oil.[24] A more elaborate method consists in squirting a chlorinated rubber solution as a stream, through nozzles, on to or beneath the surface of stirred methyl alcohol.[30] Finely divided chlorinated rubber is obtained from a solution by dispersing water in the solution. Using ammonium or potassium oleate, more water is added until a dispersion of solution in water is obtained. The solvent is then removed without breaking the dispersion by evaporation, and a finely divided product is obtained from the water.[31]

An expanded fibrous form of chlorinated rubber is prepared by heating the material under pressure which is subsequently reduced. Expansion is facilitated by the presence of liquids, such as ethyl alcohol or benzene, which are sometimes added.[32]

If a solution of chlorinated rubber is heated with decolorising charcoal, proteins and other impurities can be satisfactorily removed.[33]

Stabilisation

It has been shown already that hydrochloric acid is eliminated during chlorination of rubber, and furthermore, the chlorinated product exhibits a tendency to split off hydrochloric acid under certain conditions. Removal of hydrochloric acid and stabilisation are effected by a number of means.

Alkali salts of prussic, stearic, palmitic, or oleic acids are added to chlorinated rubber solutions. Thus to a solution of 100 parts of chlorinated rubber in 750 parts of carbon tetrachloride is added 1·3 parts of sodium stearate. After stirring at 15°–20° C. for ten hours the solvent is removed.[34] In another process stabilisation is accomplished by means of alkali substances in organic media with *p*H greater than 11.[35] The stipulated *p*H value may be obtained as in the following example. A solution of crêpe rubber in carbon tetrachloride (25–800 pts.) is boiled for six hours to remove free hydrochloric acid and 240 parts of solvent. The rubber is precipitated in methyl alcohol (560 pts.) containing 20 per cent methyl alcohol-potassium hydroxide (50 pts.) and the mixture is stirred for fifteen hours.[4] When hydroxides are the stabilisation agents they are effective at normal temperatures, but weaker alkalies require higher temperatures. An emulsion is made from 2000 c.c. of chlorinated rubber solution (18·8 per cent), 500 c.c. of water and 30 g. of calcined soda. The mixture is stirred at 80° C. for six to eight hours.[29] The soda may be replaced by alkaline or alkaline earth hydroxides, carbonates, bicarbonates or acetates.[36]

Other stabilising agents used are the ammonium or alkali bisulphites and thiosulphates, pyridine, compounds containing the ethylene oxide group, aniline, toluidine, xylidene, urea, diphenylamine and phenylene diamine.[37]

Attainment of stability is claimed by subjecting the chlorinated rubber to electro-osmotic treatment at elevated temperatures, or by maintaining it at elevated temperatures in the absence of alkali substances and appreciable amounts of metallic salts.[38]

A long list of substances which confer stability on chlorinated rubber (29–30·5 per cent chlorine) to the disintegrating action of light includes hexamethylenetetramine, dicyclohexylamine, ditetrahydrofurfurylamine, methylene aminoacetonitrile, cyclohexylamine formaldehyde, cyclohexylaminoacetonitrile, tetramethylthiuram disulphide, diphenyl guanidine and dihydroxydiphenylpropane.[39] Benzoyl peroxide is described as a preserving agent for chlorinated rubber.[40]

Becker considers that the neutralisation of the free acid, split off from chlorinated rubber, by the addition of basic substances is not satisfactory. The *p*H of the system is altered because the basic substances are removed from the sphere of action, and elimination of acid proceeds more rapidly.

Ethylene oxide or derivatives possess the property of absorbing the acid, without simultaneously causing a change in *p*H, and their use has been recommended. In illustration of the effectiveness of ethylene oxide, Becker points out that with chlorinated rubber after treatment with ethylene oxide, there were only slight signs of acid formation after heating for several days at 100° C. in the presence of light, whereas the alkali stabilised product yielded acid after only twenty minutes' exposure to these conditions.[41]

Properties

Form and Types.—Chlorinated rubber is available as fine granular powder, fibres, or porous block. It is white or cream in colour. The bulk density varies from 50 gm. per litre for the fibrous form to 350 gm. per litre for the fine powder. The packing density of finely divided chlorinated rubber is increased by subjecting it to the action of vapours of carbon tetrachloride, trichlorethylene, or toluene, at temperatures between the boiling-point of the solvent and 130° C. Finally, any occluded vapour is removed by warming or air blowing.[42] Proprietary brands are produced under the names of Alloprene, Tegofan, Tornesit, Duroprene, Herold and Pergut. Several grades of each are available, and are distinguished by the viscosities of the solutions they yield. The higher the chlorine content the lower the viscosity of the solution obtained. Other factors influence viscosity, however, such as the viscosity of the parent rubber.

Solutions of chlorinated rubber are usually a very pale straw colour and not absolutely clear. A clarity test has been devised which consists in measuring the amount of light transmitted through the solution by photoelectric means. The solid particles in suspension cause absorption of light.

Chlorine Content.—Products with low chlorine contents are unstable. The soft product containing 40 per cent chlorine ($C_{10}H_{16}Cl_3$) splits off hydrochloric acid readily. When the chlorine content is increased to 54 per cent, the product is distinctly harder, and has improved stability. Commercially available products contain about 65 per cent of chlorine, approximating to the formula $C_{10}H_{13}Cl_7$, and have maximum hardness and stability.

Solubility.—They are soluble in a wide range of solvents, including aromatic and chlorinated hydrocarbons, carbon disulphide, acetates, ethers, methyl ethyl ketone, mesityl oxide, Cellosolve, *p*-cymene, and Tetralin. Some blended solvents are also effective. Examples are turpentine 70 per cent, with solvent naphtha 30 per cent; acetone 70 per cent with hexane 30 per cent, and acetone 97 per cent with mineral spirits 3 per cent. Aromatic hydrocarbons are popular solvents for chlorinated rubber by reason of their cheapness and effectiveness. Krumbhaar has emphasised this as a disadvantage of the material, in that such strong solvents cause the lifting of undercoats during brush application.[43] Non-solvents are water, aliphatic hydrocarbons, turpentine, mineral oils, ethyl alcohol and alcohols generally, glycerol and Decalin.

TYPICAL GRADES OF CHLORINATED RUBBER

Grade.	*Viscosity (poises at 25° C. for 40 g. in 100 c.c. toluene).*
Alloprene B	1–5
,, C	5–12
,, D	12–35
,, E	35–100

Grade.	*Viscosity (poises at 20° C. for 20 % toluene soln.).*
Porgut N	0·75–0·8
,, H	0·85–1·0
,, HH	1·35–1·6

Grade.	*Viscosity (poises at 25° C. for 20 % toluene soln.).*
Tornesit 1	0·3
,, 2	1·3
,, 3	5·0

Plasticisers.—Simple solutions of chlorinated rubber yield films which have a tendency to brittleness and lack adhesion. Plasticisers and/or resins are, therefore, necessary additions. As the viscosity of solutions increases, the flexibility of the resultant films increases simultaneously.

Plasticisers include chlorinated diphenyls, chlorinated naphthalene, Cerechlor, T oil, Desavin, Softener N, Plastomoll SW, tricresyl, tritolyl, tributyl, triphenyl and tri-isobutyl phosphates, Cetamoll QU, Palatinols C, BB, HS, L and O, linseed, blown linseed, boiled linseed, perilla, soya bean, fish, oiticica, olive, tung, thermolysed tung and castor oils, dibutyl, dimethyl, diethyl, methyl cyclohexyl, benzyl butyl, and Cellosolve phthalates; Santicisers B. 16 and M. 17, Hercolyn, triethyl citrate, adipates, camphor, butyl, amyl and methyl cyclohexyl stearates; amyl and methyl Cellosolve oleates; butyl myristates, Vulkanol B; butyl phthalyl butyl, methyl phthalyl ethyl, and ethyl phthalyl ethyl glycollates; the formal of phenoxy or cresoxy-ethanol and the acetal of phenoxy-ethanol, and butyl phenoxyacetate.[44]

Compatibility.—Compatibility with resins and other-varnish ingredients is good. Chlorinated rubber blends with some alkyds, some phenol formaldehyde resins, some acrylic resins, coumarone and indene resins, vinyl resins, T.C. and A.W. 2 resins, rosin and oxidised rosin, ester gum, natural gum copals, elemi, damar, oxidised rubber, tars and bitumens. Compatibility is usually poor with alcohol soluble substances.

Stability.—The first grades of this product which appeared on the market possessed certain defects, among which was instability. By modifications in method of manufacture much of this has been eliminated.

At temperatures of the order of 150° C. chlorinated rubber begins to char and disintegrate. Continuous heating at 100° C. for 400 hours

produces a loss in weight of 5 per cent.[45] Reduction of chlorine content to the extent of 0·25 per cent occurs after heating at 100° C. for seventy-two hours, and the chlorine lost is chiefly in the combined form as hydrochloric acid.[46]

Decomposition does not assume serious proportions until 135° C. is reached. The chief decomposition product is hydrochloric acid, although pigments have an influence on type of decomposition product formed. Thus lead chromate promotes the formation of chlorine. With zinc chromate, however, chlorine is not evolved.[47]

The temperature of decomposition is determined, according to Redfarn, by noting the temperature at which a precipitate is formed, when an inert gas such as nitrogen is passed over the heated substance and into silver nitrate solution.[48] Another method of ascertaining stability is due to Rosenthal and Schultze, and consists in immersing a tube containing a solution of chlorinated rubber in xylol, in an oil bath at 100° C. A strip of Congo test paper is suspended over the surface of the solution, and the time required for the paper to turn blue over a specified area is taken as a measure of stability.[49]

In paints, stabilisers such as the oxides of zinc, magnesium and barium can be introduced to absorb free hydrochloric acid. The substitution of part of the normal pigment by sulphur is also claimed to give improved stability.[50]

Exposure to ultra-violet light of clear lacquers induces brittleness, but this can be minimised by the introduction of pigment. Ultra-violet light also causes opacity of the film to develop, but additions of benzoyl peroxide are claimed to prevent this.[51]

Solvent Resistance.—Chlorinated rubber in its normal condition resists the solvent action of petrol or alcohol. Solvent resistance can be increased by the addition of a number of complex organic compounds. Thus the chlorinated rubber is heated with piperidine pentamethylene and dimethylamine dimethyl-dithiocarbamates, the diphenyl guanidine salt of dimethyl amino-dimethyl dithiocarbamic acid, oxidation products of dithiocarbonates, thiuram mono and disulphides, tetra methyl thiuram monosulphides, thiocarbanilide, di-*o*-tolyl thiourea, mercaptobenzothiazole, with diphenylguanidine and dinitrochlorobenzene if desired. Accelerators may be present also, and these include the oxides of zinc, calcium, lead and magnesium. Insolubilising agents which may be added direct to solutions of chlorinated rubber are piperidine, methylamine, tetramethylene-diamine, urea, thiourea, dithiocarbamic acid, thiuram sulphide, mercaptothiazole, carbanilide or guanidine, or their salts and substitution products.[52]

Solvent Retention.—Chlorinated rubber films demonstrate a distinct tendency to retain solvent, and for air-drying compositions it has been suggested that the solvents used are restricted to those with boiling ranges no higher than that of xylol.[53] Because of the tendency to solvent retention, Peters has suggested that no tests should be conducted on

films until at least seven days have elapsed after application.[51] Blom has shown that retention of solvent causes marked variations in the tensile strength of a film. A film from a solution of chlorinated rubber in xylol was still plastic after drying forty hours at 35° C., and showed zero tensile strength. After subjecting it to more stringent drying conditions, i.e. twenty-four hours at 50° C., a high value for tensile strength was obtained.[55] Solvent retention also causes increased water absorption.

Chemical Resistance.—Resistance to the action of a wide range of chemicals is outstanding. Suitably prepared films resist solutions of caustic soda (5–50 per cent), caustic potash, washing soda, ammonia, ammonium nitrate (50 per cent), trisodium phosphate, and other alkaline salts, solutions of sulphuric (5–70 per cent), nitric (10 per cent), hydrochloric (10 per cent), hydrofluoric, phosphoric (85 per cent), acid salts, and organic acids such as lactic acid (5–80 per cent); bleach solutions; and gases such as chlorine, fluorine, ammonia, sulphur dioxide, hydrogen sulphide, nitric oxide and ozone.

Porosity.—Porosity can be eliminated by making additions of resins and plasticisers. A mixture of phenol formaldehyde resin and tritolyl phosphate has been claimed to be effective. Other phosphoric esters, and natural, vinyl and cyclohexanone resins have been suggested to reduce porosity also.[56] A permeability test devised by Blom, involves coating an iron rod with the chlorinated rubber composition, and immersing it in a ½ per cent slightly acidic solution of copper sulphate. In about four hours spots of copper appear at every pore. Alternatively, clear varnishes may be applied to a piece of glass, and after drying for twenty-four hours it is immersed in water. Enlargement of the pores occurs and they become visible.[57]

Inflammability.—Like most chlorinated organic compounds, chlorinated rubber has excellent combustion resisting properties. Its decomposition temperature has been included already. On heating, chlorinated rubber does not glow or burst into flames. The vapours evolved during the disintegration, consequent upon heating, contain substantial amounts of hydrochloric acid, and this serves to extinguish any flames in the vicinity. By reason of the solvent retention of chlorinated rubber, the use of chlorinated hydrocarbons like chloroform and carbon tetrachloride in non-inflammable finishes is, therefore, distinctly advantageous.

Electrical Properties.—Unplasticised films have the high dielectric strength of 2300 volts per mil, a value which is substantially maintained even under moist conditions. Plasticisation causes a reduction in this figure. A film containing 20 per cent of dibutyl phthalate has a dielectric strength at 25° C. of 1000 volts per mil.

Non-penetration.—Chlorinated rubber films show little tendency to penetrate porous surfaces such as wood, paper or fabrics. Since they remain chiefly at the surface the gloss produced is good.

Hardness.—The films obtained are very hard, exhibiting good scratch and abrasion resistance. They may be used as rubbing finishes.

Effect on Dry.—The incorporation of chlorinated rubber into oleo-resinous varnishes causes an appreciable improvement in the speed of dry. In fact, some have suggested a blend of linseed oil and chlorinated rubber as being a satisfactory substitute for tung oil, under certain conditions.

There are two methods of incorporating the chlorinated rubber into varnishes. It may be dissolved in the hot oil-resin mix, but great care is essential to accomplish this satisfactorily. The temperature should not be so high as to cause decomposition, and should not be allowed to exceed 100° C. Furthermore, the rubber should be added slowly with constant stirring. Alternatively, it may be added as a solution to the finished varnish, in which case the solvent of the varnish should be a solvent for the chlorinated rubber also. Of the two methods the latter is generally considered to be preferable.

Chlorinated rubber is claimed also to effectively increase the speed of drying of alkyds, in addition to improving their hardness.

Cobwebbing.—For reasons already mentioned, the use of volatile solvents with chlorinated rubber is advocated, and this accentuates the marked tendency of this material to cobweb, whether applied by brush or spray. One way of reducing cobwebbing is to replace part of the low boiling aromatic solvent by Tetralin and dipentene. If oxidised rubber is added to chlorinated rubber in substantial quantities, cobwebbing is eliminated. Addition of sulphurised oils is stated to facilitate application of chlorinated rubber paints.[58] Coolahan suggests that for spraying, chlorinated rubber paints should have a viscosity of 0·4 poises and contain 12–14 per cent solids.[59]

Tensile Strength.—This property varies considerably with the viscosity of the solution given by the chlorinated rubber and with the type and amount of plasticiser. Baxter has recorded that low viscosity products have correspondingly low tensile strengths, although over a wide range of higher viscosity rubbers the tensile strengths were higher but practically constant. Two examples may be quoted to illustrate how even slight over-plasticisation results in substantial reduction in film strength. With 21 per cent dibutyl phthalate the tensile strength is 6000–7000 lb. per sq. in., but when increased slightly to 23 per cent, the tensile strength is reduced to the surprisingly low figure of 1500 lb. per sq. in.[60] Alloprene plasticised with similar amounts of Cerechlor, tricresyl phosphate, and dibutyl phthalate gave tensile strengths of 4500, 3700 and 3300 lb. per sq. in. respectively.[61] Pigment content is also critical from the point of view of tensile strength, and Wolff and Zeidler suggest 40–50 per cent.[62]

Thermoplasticity.—Chlorinated rubber becomes plastic on heating above 80° C., and because of this property its direct application has been suggested. It has also been utilised in moulding compositions.

Water Resistance.—Moisture permeability of chlorinated rubber is low. A one per cent loss of chlorine occurred when chlorinated rubber was

heated at 97° C. in the presence of water. Decomposition is substantially greater on heating in the presence of water than in its absence.[46] A temperature of 65° C. is stated to be critical for chlorinated rubber in contact with water.[51]

Preparation of Films.—A surface is first coated with a material based on glue, gelatin, or sodium silicate. A solution of chlorinated rubber is then applied and the solvent evaporated. The resultant film has no affinity for the first coating material and can be stripped off. This can be facilitated by dissolving out the first coating with water.[63]

Uses

Because of the versatility of chlorinated rubber, carefully formulated compositions containing it are used in many industries.

Chemical Resistant Finishes.—It is encountered most frequently in this type of finish. It is obvious that plasticisers and pigments which may be used should have a chemical resistance comparable with that of the chlorinated rubber. Improved resistance to acids, alkalies and salts is obtained if the chlorinated rubber composition is plasticised with sulphur derivatives of toluene or xylene produced in the presence of aluminium chloride.[64] Chlorinated rubber paints and varnishes, because of alkali resistance, are suitable for use on concrete, cement, cement-asbestos boards, stucco, brick and plaster, in laundries and on domestic washing machines. For this latter purpose the protective film must be resistant to boiling soap solution and the active oxygen from sodium perborate. A formula satisfying these conditions consists of chlorinated rubber, plasticiser Albertalate 1246B and certain pigments, according to the finish desired.[65] With new concrete work it is claimed that chlorinated rubber products may be applied without waiting for the concrete to age.

A composition derived from chlorinated rubber and linseed or tung oil, with other plasticisers and pigments, is used to provide a coating after stoving, resistant to corrosive liquids and war gases.[66]

A thermoplastic acid resisting luting or jointing compound contains chlorinated rubber (65 per cent chlorine), chlorinated paraffin wax (45–52 per cent chlorine) and chlorinated naphthalenes. Small amounts of acid neutralising agents such as lime or chalk may be added, as well as asbestos filler.[67]

A similar composition for which good chemical resistance is claimed is produced from chlorinated rubber and chlorinated paraffin wax (30 per cent chlorine) in a suitable solvent. The proportion of wax to rubber varies from 8 to 25 parts for 20 parts of rubber.[68]

A varnish resistant to acid and alkali comprises, chlorinated rubber, oxidised drying oil, with xylol, turpentine and Tetralin as thinner.[69] An acid and alkali resisting lacquer is made by adding linseed, tung, rapeseed or corn oil, to a chlorinated rubber solution and vulcanising the oil by means of sulphur or sulphur chloride.[70]

Varnish Constituents

Another chemical resistant coating involves chlorinated rubber 40 parts, toluol and xylol 60 parts each, butylated diphenyl 12 parts, and titanium dioxide 20 parts.[71]

Chemically resistant chlorinated rubber finishes may be utilised in coating the inside of swimming pools and water tanks to resist the action of chlorine, the inside of chemical tanks generally, tunnels, structural metal work embedded in concrete to prevent attack by the alkali, plant in Gas, Salt, Acid and Alkali works, electroplating equipment, bleaching plant, dyehouse plant, aluminium spinning spools to resist acids and dipping solutions, interior of ice factories to resist ammonia, interior of slaughter houses to resist fatty acids and brine for pickling, interior of accumulator factories and electrical storage rooms to resist acid and other vapours, interior of vinegar works to resist acid vapours, interior of breweries to resist ammonia and gases from fermentation, interior of pulp and paper mills to resist acids, alkalies, bleach solutions and chlorine gas, interior of galvanising works to resist acid vapours from pickling vats, the interior of food pickling factories to resist acid vapours and salt solutions; and on tank waggons for corrosive liquids.

Anti-corrosive Finishes for Iron and Steel.—Chlorinated rubber products are sometimes used in anti-corrosive finishes for protecting iron and steel work against corrosion, due to the influence of air, moisture, and sea-water. In this respect, Strauss emphasises the importance of using chlorinated rubbers which are neutral. The presence of free hydrochloric acid causes an immediate attack of the metal surface, and in paints may react with pigments forming water soluble chlorides which stimulate rusting.[72]

When iron pipes, which are to be placed underground, have to be protected against corrosion, it is suggested that they receive a preliminary treatment with phosphoric acid. The etched surface obtained not only provides improved corrosion resistance, but also a satisfactory key for the subsequent application of the chlorinated rubber paint.

A blend of chlorinated rubber, resin and plasticiser is stated to be an excellent anti-corrosive coating for steel. The common bituminous coatings which are used for this purpose give better results after the inclusion of some chlorinated rubber.[73]

A primer for metals resistant to sea-water contains substantially chlorinated rubber 20 parts, chlorinated diphenyl 3 parts, benzyl naphthalene 2 parts, white lead 12 parts, micaceous iron ore 10 parts, and solvent 52 parts.[74]

Lacquers and Media for Other Metals.—Protective lacquers for many metals are formulated on chlorinated rubber. Excellent protection is afforded to aluminium,[75] for example.

A pigmented lacquer is made from chlorinated rubber, pigments, and an unsaponifiable plasticiser selected from chlorinated naphthalenes and diphenyls, aralkylated naphthalenes, compounds resulting from the reaction of sulphur with benzene homologues in the presence of aluminium

chloride, and coumarone resins. In addition to these plasticisers mineral oils may be present.[76]

Chlorinated rubber lacquers or paints, for duralumin and electron metal, contain ester gum, an ordinary plasticiser and/or drying or non-drying oils. The solvents are the aromatic hydrocarbons, benzene, toluene or xylene, or blends with cyclohexanone and ethyl or butyl acetates. Pigments are chosen from aluminium powder, zinc oxide, titanium dioxide and iron oxides; fillers from china clay, talc, ground shale, and quartz dust.[77]

A lacquer for light metals is plasticised with phosphates, phthalates, olive or castor oil.[78] A paint for light metal aeroplane wings as given by Strauss (*loc. cit.*) contains chlorinated rubber 200 parts, toluol 300 parts, xylol 300 parts, tricresyl phosphate 30 parts, tributyl phosphate 20 parts, and oxide of iron 100 parts.

A process for treating light metals consists of a first coating of a polyvinyl carboxylic ester composition followed by a chlorinated rubber lacquer.[79]

Chlorinated rubber finishes adhere well to anodically oxidised metals.

Fireproof Finishes.—These are utilised on aeroplanes, ships, wood, fabrics and electric cables. The fire-resisting properties of chlorinated rubber are put to best advantage when used with fire-resisting plasticisers such as chlorinated diphenyls and phosphates.

A typical composition consists of chlorinated rubber 20 parts, rubber 100 parts, chlorinated diphenyl (59 per cent chlorine) 80 parts, sulphur 3·2 parts, accelerator 3 parts, anti-perishing agent 1·5 parts, kieselguhr 80 parts, and zinc oxide 15 parts.[80] A non-inflammable lacquer for impregnating textiles is chlorinated rubber solution containing cellulose and phosphoric esters.[81] Some finishes rely upon the presence of pigments to assist in conferring fire resistance. Thus a substantial amount of antimony oxide is incorporated in a chlorinated rubber solution in toluene, plasticised with stand oil, and containing, in addition, white lead and bone black.[82]

A mixture of chlorinated rubber 1 part, and chlorinated paraffin (40–50 per cent chlorine) 3–10 parts, in which is worked chalk and cork or wood dust, with plasticisers if desired, is used as a non-inflammable floor covering.[83]

Leather Finishes.—A leather finish with good adhesion is produced from a solution of chlorinated rubber in xylol, plasticised with tricresyl phosphate or dibutyl phthalate and synthetic resin.[84]

Emulsions sometimes provide satisfactory dressings for leather, and the following is an example. An emulsion is made from water, casein, borax and ammonia, with chlorinated rubber, linseed oil and drier.[85]

Paper and Fabric Finishes.—The waterproofing and non-penetrating properties of chlorinated rubber are exploited in finishes for these materials.

Fabric is made waterproof by impregnation with a composition comprising chlorinated rubber, ordinary rubber, shellac and plasticiser.[86]

A special coated paper employs a blend of chlorinated rubber 40–50

per cent, with paracoumarone and a glyceryl abietate to the extent of 25–38 per cent, plasticiser 15–21 per cent and paraffin wax 2–7 per cent. A similar composition for porous surfaces is derived from high viscosity chlorinated rubber, plasticiser, resin, paraffin wax and a volatile solvent. The resin is either damar or alkyd resin. Another impregnating solution for paper contains, in addition to chlorinated rubber, tricresyl phosphate and coumarone resin dissolved in naphtha.[87]

Chlorinated rubber acts as a surface tension increasing agent in a size for paper and fabric, based on polyvinyl resin.[88]

A dispersion of chlorinated rubber 10 parts, tricresyl phosphate 1 part, and nigrosine to colour, in water 20 parts, is used to provide a flexible coating for paper or fabric.[89]

Anti-Fouling Paints.—The good sea-water resistance of chlorinated rubber has suggested its use in anti-fouling paints for ships and buoys. This material also prevents marine growth, a property which may be coupled with that of more potent poisons, of which diphenyl arsine is an example.[90]

Other Uses.—The use of chlorinated rubber in moulding compositions has been referred to already. A solution of rubber in carbon tetrachloride is mixed with water. It is then chlorinated by stirring in a chlorine solution in carbon tetrachloride. Wood flour, titanium pigment, and spirit blue are added and the whole evaporated, powdered and dried. The dry powder is used for moulding.[91]

A shock resistant coating is based on chlorinated rubber and powdered carborundum.[92] Hard abrasion resisting traffic paints utilise chlorinated rubber.

Chlorinated rubber is resistant to the formation of moulds or mildew, and is thus used in preservative finishes for coating-glue, gelatin or photographic plants.

Great improvements in properties are obtained when chlorinated rubber or rubber hydrochloride is added to road tars.[93]

High viscosity chlorinated rubber is used to provide flexible, non-inflammable, water and chemical resistant coatings with good electrical properties for cables.

Solutions of chlorinated rubber have been used as media for metallic paints or for luminous paints, incorporating calcium sulphide.[94]

By reason of its insolubility in alcohol and petrol, chlorinated rubber is found in finishes to resist these solvents.

Fluorinated Rubber

Very little information is available about this halogenated rubber. It may be prepared, however, by passing fluorine into a solution of rubber in carbon tetrachloride. Or rubber may be treated directly with fluorine, with care, to avoid combustion. The reaction is controlled by conducting it below 0° C., and by diluting the fluorine with up to ten times its own volume of air, carbon dioxide or nitrogen.[95]

Rubber Hydrochloride

When hydrochloric acid reacts with rubber, one acid molecule adds on for each isoprene unit.

The reaction may be conducted by saturating a chloroform solution of rubber with hydrochloric acid, and allowing the reactants to remain in contact for twelve hours. A similar method consists in passing the acid gas into a 6 per cent solution of rubber in benzene at 10° C. for six hours. The whole is allowed to stand for twenty hours.[96] The rubber hydrochloride is obtained either by removing the solvent or by precipitation with alcohol. It is a soft elastic substance decomposing on heating at 145° C., but is claimed to possess useful film-forming properties.[97] Vulcanised rubber hydrochlorides have been reported.

Oximes have been suggested as suitable ageing inhibitors, and the use of two, methyl ethyl ketoxime and heptaldoxime, has been protected.[98]

Compositions have been made from rubber hydrochloride and ester gum, shellac or coumarone. Sulphur is incorporated in addition, if desired.[99]

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TEMPERATURES—CENTIGRADE TO FAHRENHEIT CONVERSION TABLE

Centigrade. °C.	*Fahrenheit.* °F.	*Centigrade.* °C.	*Fahrenheit.* °F.
0	32·0	175	347·0
5	41·0	180	356·0
10	50·0	185	365·0
15	59·0	190	374·0
20	68·0	195	383·0
25	77·0	200	392·0
30	86·0	205	401·0
35	95·0	210	410·0
40	104·0	215	419·0
45	113·0	220	428·0
50	122·0	225	437·0
55	131·0	230	446·0
60	140·0	235	455·0
65	149·0	240	464·0
70	158·0	245	473·0
75	167·0	250	482·0
80	176·0	255	491·0
85	185·0	260	500·0
90	194·0	265	509·0
95	203·0	270	518·0
100	212·0	275	527·0
105	221·0	280	536·0
110	230·0	285	545·0
115	239·0	290	554·0
120	248·0	295	563·0
125	257·0	300	572·0
130	266·0	305	581·0
135	275·0	310	590·0
140	284·0	315	599·0
145	293·0	320	608·0
150	302·0	325	617·0
155	311·0	330	626·0
160	320·0	335	635·0
165	329·0	340	644·0
170	338·0	345	653·0
		350	662·0

ATOMIC WEIGHTS

Element.	Symbol.	Atomic weight (1933).*
Actinium	Ac	(227)
Alabamine	Ab	(221)
Aluminium	Al	26·97
Antimony, stibium	Sb	121·76
Argon	A	39·944
Arsenic	As	74·93
Barium	Ba	137·36
Beryllium, glucinum	Be	9·02
Bismuth	Bi	209·00
Boron	B	10·82
Bromine	Br	79·916
Cadmium	Cd	112·41
Calcium	Ca	40·08
Carbon	C	12·00
Cerium	Ce	140·13
Cesium	Cs	132·81
Chlorine	Cl	35·457
Chromium	Cr	52·01
Cobalt	Co	58·94
Columbium, niobium	Cb	93·30
Copper	Cu	63·57
Dysprosium	Dy	162·46
Erbium	Er	167·64
Europium	Eu	152·00
Fluorine	F	19·00
Gadolinium	Gd	157·30
Gallium	Ga	69·72
Germanium	Ge	72·60
Gold, aurum	Au	197·20
Hafnium, celtium	Hf	178·60
Helium	He	4·002
Holmium	Ho	163·50
Hydrogen	H	1·0078
Illinium	Il	(146)
Indium	In	114·8†
Iodine	I	126·92
Iridium	Ir	193·10
Iron, ferrum	Fe	55·84
Krypton	Kr	83·70
Lanthanum	La	138·92
Lead, plumbum	Pb	207·22
Lithium	Li	6·940
Lutecium	Lu	175·00
Magnesium	Mg	24·32
Manganese	Mn	54·93
Masurium	Ma	
Mercury, hydrargyrum	Hg	200·61
Molybdenum	Mo	96·00
Neodymium	Nd	144·27
Neon	Ne	20·183
Nickel	Ni	58·69
Nitrogen	N	14·008

* *J. Amer. Chem. Soc.*, March, 1925, Feb. 1933.
† 114·76 reported by Baxter and Alter, *ibid.*, **55**, 1943, 1933.

ATOMIC WEIGHTS—*Continued*

Element.	Symbol.	Atomic weight (1933).*
Osmium	Os	190·80
Oxygen	O	16·000
Palladium	Pd	106·70
Phosphorus	P	31·02
Platinum	Pt	195·23
Polonium	Po	(210)
Potassium, kalium	K	39·10
Praseodymium	Pr	140·92
Protoactinium	Pa	
Radium	Ra	225·97
Radon, niton	Rn	222·0
Rhenium	Re	186·31
Rhodium	Rh	102·91
Rubidium	Rb	85·44
Ruthenium	Ru	101·70
Samarium	Sm, Sa	150·43
Scandium	Sc	45·10
Selenium	Se	79·20
Silicon	Si	28·06
Silver, argentum	Ag	107·880
Sodium, natrium	Na	22·997
Strontium	Sr	87·63
Sulphur	S	32·06
Tantalum	Ta	181·40
Tellurium	Te	127·50
Terbium	Tb	159·20
Thallium	Tl	204·39
Thorium	Th	232·12
Thulium	Tm	169·40
Tin, stannum	Sn	118·70
Titanium	Ti	47·90
Tungsten, wolframium	W	184·00
Uranium	U	238·14
Vanadium	V	50·95
Virginium	Vi	(224)
Xenon	Xe	131·30
Ytterbium	Yb	173·50
Yttrium	Y	88·92
Zinc	Zn	65·38
Zirconium	Zr	91·22

* *J. Amer. Chem. Soc.*, March 1925, Feb. 1933.

CONSTANTS OF SYNTHETIC RESINS †

The constants of synthetic resins are given in the following order :..

1. Acrylic resins.
2. Alkyd resins.
3. Cashew nut shell liquid resins.
4. Coumarone resins.
5. Maleic anhydride resins.
6. Melamine-formaldehyde resins.
7. Miscellaneous resins.
8. Phenolic resins (unmodified).
9. Phenolic resins (modified).
10. Polystyrene resins.
11. Silicone resins.
12. Spirit soluble resins.
13. Urea-formaldehyde resins.
14. Vinyl resins.
15. Zinc resinates.

ABBREVIATIONS

(FOR CONSTANTS OF SYNTHETIC RESINS)

S. pt. = Softening point.
F. pt. = Fusion point.
Fl. pt. = Complete fluidity.
C.S. = Completely soluble.
C.S.H. = Completely soluble hot.
P.S. = Partly soluble.
P.S.H. = Partly soluble hot.
I.S. = Insoluble.
N.C. = Nitrocellulose.

CONSTANTS OF SYNTHETIC RESINS: ACRYLIC RESINS

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
Acryloid A. 10	30 % solids in cellosolve acetate	110° C. approx. S. Pt. for film		C.S. aromatic hydrocarbons, except for A. 10, chlorinated hydrocarbons, ketones, esters, ether alcohols, ether esters	1·03	In surface coatings where water white colour, flexibility, electrical resistance and resistance to ozone, mineral and animal oils, dilute acids and alkalies, are advantageous. Heat resisting paints, fume resistant enamels, protective metal coatings, luminous paints, textile and paper finishes, electrical insulating varnishes, anti-fouling paints and shatter resisting glass.
ACRYLOID B. 7	20 % solids in ethylene dichloride	40°–58° C. S. Pt. for film			1·22	
ACRYLOID B. 72 and B. 73	40 % solids in toluol	35°–55° C. S. Pt. for film		I.S. alcohols and petroleum hydrocarbons except for F. 10 which tolerates limited amounts	0·97	
ACRYLOID C. 10	20 % solids in ethyl acetate	10°–25° C. S. Pt. for film			0·96	
ACRYLOID F. 10	40 % solids in Solvesso No. 3	15°–50° C. S. Pt. for film			0·91	
Bedacryl 122X	Polymethacrylic ester (40 % soln. in xylol)		6–9	C.S. aromatic hydrocarbons, esters, butanol, turpentine P.S. white spirit I.S. alcohol	0·93	High gloss, flexible, non-yellowing, durable, air-drying or stoving lacquers.

BEDACRYL 144 TL	Polymethacrylic ester (50 % soln. in toluol)			C.S. aromatic hydrocarbons, esters, ketones, cellosolve P.S. butanol, turpentine	0·98	Highly flexible and elastic films. Rubber lacquers.

CONSTANTS OF SYNTHETIC RESINS: ALKYD RESINS

Paralac 11	Drying oil alkyd	Plastic	5–9	C.S. in most solvents, including white spirit. Insoluble in alcohols		Coach finishes. Quick air-drying and stoving industrial finishes.
PARALAC 11W	55 % soln. of Par. 11 in white spirit					
PARALAC 11X	60 % soln. of Par. 11 in xylene					
PARALAC 12X	Oil modified. 60 % soln. in xylol	Liquid	3–7	C.S. aromatic hydrocarbons, tetralin, decalin, turps, petroleum hydrocarbons, ketones, esters, Cellosolve, diacetone alcohol, pine oil, cyclohexanol, dipentene	1·01	Low bake stoving whites.
PARALAC 14	Drying oil alkyd	Plastic	4–8	C.S. in most solvents, including white spirit		Decorative finishes of high durability. Particularly for non-yellowing indoor white enamels.
PARALAC 14W	70 % soln. of Par. 14 in white spirit				0·975	
PARALAC 15	Drying oil alkyd		12–19	C.S. mineral spirits, turpentine	1·055	Non-yellowing brushing decorative finishes. Printing inks.
PARALAC 15T	As 15 but 20 % turpentine				1·010–1·025	
PARALAC 15W	75 % soln. of Par. 15 in white spirit				0·969 0·977	

† All the resins listed are not necessarily available. Some have been deleted from manufacturer's lists, but they are still temporarily included in these tables for they may figure in old formulations, and some information on their properties may assist in finding improved types. Because research is always continuing, the latest information on existing types of resin, or types introduced after publication, or inadvertently omitted, should be obtained by applying directly to the manufacturers concerned.

* The melting points quoted in these tables are not strictly comparative. They vary according to the methods used and these are not always disclosed by the manufacturer. Where methods are not indicated the figures should be used with caution.

CONSTANTS OF SYNTHETIC RESINS: ALKYD RESINS—*Continued*

Reference.	Remarks.	M.Pt.	Acid Value.	Solubility.	S.G.	Recommended Uses.
PARALAC 16	Drying oil alkyd	Plastic solid	8–12	C.S. aromatic hydrocarbons, etc. P.S. white spirit		Stoving and air-drying industrial finishes. Metal primers.
PARALAC 16X	60 % soln. of Par. 16 in xylene					
PARALAC 17	Drying oil alkyd		7–10	C.S. mineral spirits, turpentine	1·045–1·055	Brushing air-drying finishes, in conjunction with 18T. Printing inks. Gloss paints. Primers for anti-corrosive finishes.
PARALAC 18	Drying oil alkyd	Plastic	20–30	C.S. aromatic or hydro-aromatic hydrocarbons	1·094	Durable air-drying spray finishes. Primers. Durable nitrocellulose lacquers. Reinforcing resin for gloss paints.
PARALAC 18X	As 18 but 40 % xylol				0·986–0·996	
PARALAC 18T	As 18 but 47 % turpentine				0·965–0·985	
PARALAC 18BA	As 18 but 30 % butyl acetate				1·01–1·03	
PARALAC N18	Drying oil alkyd	Plastic	2–7	C.S. aromatic hydrocarbons P.S. white spirit		Similar uses to Paralac 18 but will tolerate basic pigments.
PARALAC N18X	60 % soln. of Par. N18 in xylene				0·986 0·996	
PARALAC N18T	53 % soln. of Par. N18 in turpentine				0·965 0·985	
PARALAC 19	Drying oil alkyd	Plastic	35–45	C.S. aromatic or hydro-aromatic hydrocarbons	1·135	Stoving finishes. Metal primers. Nitrocellulose lacquers.
PARALAC 19X	As 19 but 40 % xylol				1·015–1·030	

PARALAC 20 .	Drying oil alkyd		67–76	C.S. aromatic hydrocarbons	1·206	Rapid hardening low bake spray or dipping finishes. Suitable for whites.
PARALAC 20XB .	55 % soln. of Par. 20 in xylene/butanol				1·035 1·055	
PARALAC 21 .	Drying oil alkyd	67°–76° C.	56–72	C.S. aromatic hydrocarbons		Rapid hardening low bake spray or dipping finishes.
PARALAC 285X .	Modified alkyd free *from drying oils*, rosins or phenolic resins, with 50 % xylol		40–54	C.S. ketones, esters, lower aromatic hydrocarbons, higher alcohols	0·997–1·007	Plasticiser for 2001. Nitrocellulose lacquers.
PARALAC 385 .	Modified alkyd free from drying oils, rosin or phenolic resins	69°–79° C.	30–50	C.S. ketones, esters, mixtures of alcohols and aromatic hydrocarbons P.S. alcohols I.S. hydrocarbons	1·28	Nitrocellulose and benzyl cellulose finishes. Durable and light fast.
PARALAC 585 .	As 385	62°–70° C.	18–28	C.S. ketones, esters, aromatic hydrocarbons P.S. Alcohols	1·00–1·01 (50 % soln. in toluene)	Non-rubbing durable nitrocellulose lacquers.
PARALAC 585X .	45 % soln. of Par. 585 in xylene				0·987 0·997	
PARALAC 685 .	As 385	Plastic	50–62	C.S. ketones, esters, lower aromatic hydrocarbons, higher alcohols I.S. white spirit, turpentine	1·04–1·05 (65 % soln. in toluene)	Resin plasticiser for wood or metal nitrocellulose lacquers. Durable, water resistant.
PARALAC 1001 .	Thermohardening, free from drying oil	68°–84° C.	160–190	C.S. ketones, alcohols, esters, aqueous ammonia I.S. hydrocarbons	1·38	Bond for asbestos, mica, etc.
PARALAC 1101 .	As 1001	95°–105° C.	130–160	Similar to 1001 but generally less soluble	1·39	Bond for asbestos, mica, etc.
PARALAC 1201 .	As 1001	110° C.	125 approx.	Similar to 1101 but generally less soluble	1·39	Bond for asbestos, mica, etc.
Beetle RESIN RP. 8 . (BA. 502)	Non-drying oil modified alkyd, with 40 % xylol		25–30	C.S. mixture of aromatic hydrocarbons and alcohols	1·05	Plasticising resin for urea formaldehyde resins. Nitrocellulose lacquers.

CONSTANTS OF SYNTHETIC RESINS: ALKYD RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
Bedesol H .	Water soluble alkyd		Almost neutral in water	C.S. water, aqueous acetone, aqueous alcohol		Stiffening agent in hat proofing, etc.
BEDESOL 52 .	Rosin modified alkyd	102°–116° C.	13–19	C.S. aromatic hydrocarbons, turpentine, ketones, esters, and higher alcohols	1·06 as 70 % soln. in toluene	Nitrocellulose furniture lacquers, sanding sealers. In drying oil Paralacs to improve hardness. Water resistant.
BEDESOL 72 .	Alkyd modified with natural resin	145° C.	28	C.S. aromatic hydrocarbons, esters, sextol P.S. aliphatic hydrocarbons I.S. methylated spirit		For nitrocellulose lacquers, clear and pigmented wood lacquers, sealers, gravure inks. Gloss paints.
BEDESOL 199 .	Alkyd modified with phenolic resin		30 approx.	C.S. turps, aromatic hydrocarbons P.S. petroleum hydrocarbons		For blending with alkyds to improve speed of air-drying, speed of stoving, water, acid and alkali resistance, hardness; to prevent penetration and webbing.
BEDESOL 199SN .	65 % soln. of Bed. 199 in solvent naphtha				1·02 1·03	
BEDESOL 199W .	50 % soln. of Bed. 199 in white spirit				0·905 0·915	
Lewisol 2 . .	Modified alkyd resin	132°–134° C.	10–12			For non-yellowing, pale, rapid drying varnishes or media for interior or exterior. White stoving enamels. Compatible with zinc oxide.
LEWISOL 2L .	Modified alkyd resin	134°–138° C.	10–12			
LEWISOL 3 . .	Modified alkyd resin	94°–98° C.	14–16			Nitrocellulose lacquers as a plasticising resin. Good colour retention and gloss.

LEWISOL 18 .	Modified alkyd resin	116°–120° C.	12–14			Sanding sealers. Durable water resistant varnishes for interior and exterior. White stoving enamels.
Durecol NAZ .	Alkyd modified by addition of abietic acid			C.S. mixtures of aromatic hydrocarbons and alcohols, ethyl esters I.S. oils		
DURECOL NAX .	Alkyd modified by addition of abietic acid			As NAZ but also C.S. in butyl esters		For nitrocellulose lacquers. Good light fastness.
DURECOL NAB .	Alkyd modified by addition of abietic acid			As NAZ but C.S. aromatic hydrocarbons		
DURECOL NHF .	Alkyd modified with linseed oil			C.S. aromatic hydrocarcarbons I.S. petroleum or terpenic hydrocarbons		Glyceryl phthalate content 60 %. Spraying baking enamels.
DURECOL NHL .	Alkyd modified with linseed oil			As NHF but better solubility in petroleum hydrocarbons		Glyceryl phthalate content 50 %. Spraying air-drying enamels.
DURECOL NHW .	Alkyd modified with linseed oil	Viscous		C.S. white spirit and turps		Glyceryl phthalate content 40 %. Brushing air-drying enamels.
DURECOL NHWS .	Alkyd modified with linseed oil	Less viscous		C.S. white spirit and turps		Glyceryl phthalate content 40 %. Brushing air-drying enamels, compatible with zinc white.
DURECOL NHB .	Alkyd modified with linseed oil			C.S. white spirit and turps		Glyceryl phthalate content 30 %. Slower air-drying films than NHW or NHWS Good brushing paints. Compatible with zinc white.
DURECOL NHJ .	Alkyd modified with linseed oil					
DURECOL NOA .	Alkyd modified with oils other than linseed oil			C.S. aromatic hydrocarbons		Glyceryl phthalate content 50 %. Contains tung oil. More water resistant than NH series. Spraying enamels.

CONSTANTS OF SYNTHETIC RESINS: ALKYD RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
DURECOL NOE .	Alkyd modified with oils other than linseed oil			More soluble than NOA		Glyceryl phthalate content 25 %, + 10 % modifying resin. Contains tung oil. More bodied and more brilliant enamels than NOA.
DURECOL NOD .	Alkyd modified with oils other than linseed oil					Glyceryl phthalate content 40 %. More flexible than NOA and NOE.
DURECOL NOR .	Alkyd modified with oils other than linseed oil					Glyceryl phthalate content 44 %. For flexible stoving finishes, 130° C./45 mins. For rubber and leather goods.
DURECOL NRN .	Alkyd modified with non-drying oils					Glyceryl phthalate content 60 %. As a resin-plasticiser for nitrocellulose.
DURECOL NRS .	Alkyd modified with non-drying oils			C.S. all organic solvents except alcohols P.S. oils		Glyceryl phthalate content 35 %. Poor drying properties. Non-yellowing to light or stoving up to 130° C. Special for zinc white enamels. Good water-resistance.
DURECOL NRB .	Alkyd modified with non-drying oils					For white, air-drying or baking enamels of good light resistance. Stoves 120°–140° C.
Glycopal N .		A hard resin				Light fast lacquers and for stoving.
GLYCOPAL NA .			Rather pronounced	C.S. ammonia and triethanolamine		
GLYCOPAL NS .	The alkaline salt of NA		Neutral	C.S. hot water		

GLYCOLAC NE	Alkyd modified by drying oils and natural resins			Limited. C.S. aromatic hydrocarbons		Rapid air-drying or baking enamels for spraying.
GLYCOLAC NS	Alkyd modified by drying oils and natural resins			As NE		As NE but slower drying and more water resistant.
GLYCOLAC NW	Alkyd modified by drying oils and natural resins			C.S. white spirit and turps + aromatic hydrocarbons or butyl alcohol		Quick drying brushing interior enamels of good gloss.
Teglac 15	Alkyd modified with natural resin acid	86°–91° C.	12–18	C.S. usual lacquer solvents	1·14	Clear pigmented wood lacquers and sanding sealers. Nitrocellulose lacquers.
TEGLAC Z–152	Alkyd modified with natural resin acid	140°–150° C.	27–37	C.S. usual lacquer solvents	1·14	Interior clear and pigmented lacquers. Nitrocellulose lacquers. Binder for intaglio inks. Oleoresinous varnishes.
TEGLAC Z–154	Alkyd modified with natural resin acid	110°–115° C.	12–22	C.S. usual lacquer solvents	1·11	Cheap sanding sealers. Interior clear and pigmented lacquers. Softer and slower drying than Z–152.
TEGLAC 161	Alkyd modified with natural resin acids	140°–150° C.	27–37	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons	1·14	For cooking with drying oils. Pale varnishes for interior woodwork, furniture, etc. Pale tin-plate varnishes. For nitrocellulose lacquers. Sanding sealers.
Alprokyd 525V	Glyceryl phthalate resin and phenolic resin — 47% Fatty oil — 53% 70% soln. in xylol		<25 (solid resin)	C.S. aromatic hydrocarbons I.S. Aliphatic hydrocarbons and drying oils	1·125 (solid resin)	Non-drying. Leather finishes. Nitrocellulose lacquers. Paper lacquers.
ALPROKYD 525VX	50 % soln. in xylol of non-drying oil modified alkyd	Liquid	40–47	C.S. ketones, esters, hydrocarbons, higher alcohols	0·999–1·010	Plasticiser for urea-formaldehyde resins. Nitrocellulose lacquers.
ALPROKYD 607P	Drying oil alkyd	Plastic	<12	C.S. aromatic hydrocarbons, white spirit, etc.		Non-yellowing, brushing decorative finishes.

CONSTANTS OF SYNTHETIC RESINS: ALKYD RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
ALPROKYD 615ZX	Drying oil alkyd 60 % soln. in xylol	Liquid	5–9	C.S. aromatic hydrocarbons, white spirit, etc.		Coach finishes. Quick air-drying and stoving industrial finishes.
ALPROKYD 624J .	Drying oil alkyd			C.S. aromatic hydrocarbons		Industrial stoving finishes. Primers.
ALPROKYD 626L . (high viscosity)	70% soln. in xylol. Glyceryl phthalate resin 40% Fatty oil 60%		<20 (solid resin)	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons and drying oils	1·090 (solid resin)	Air-drying. Spraying and dipping finishes. Water resistant, durable and good colour retention.
ALPROKYD 626L . (low viscosity)	Pure resin as above		<20	S. aliphatic hydrocarbons P.S. drying oils	1·075	Air-drying. For combination with stand oils by cooking. Wrinkle finishes with tung oil.
Aroplaz 900 .	50 % solids in white spirit, medium to short oil, oxidising		6–10 (resin)			Enamel media. Petroleum pump finishes, oxide primers, roller coating, motor-car, wood, and paper finishes.
Aroplaz 900 .	70 % solids in toluol as 900 above		6–10 (resin)			Enamel media. Petroleum pump finishes, oxide primers, roller coating, motor-car, wood, and paper finishes.
AROPLAZ 905 .	50 % solids in toluol, very short, non-oxidising		10–15 (resin)			Hard rubbing lacquers. Paper coatings. Very cold check resistant.
AROPLAZ 905 .	50 % solids in xylol, as 905 above		10–15 (resin)			
AROPLAZ 930 .	Short, non-oxidising		4–6			Plasticiser for N.C. For motor-car, wood, paper and rubber lacquers.
AROPLAZ 935 .	50 % solids, 25 % dipentene, 25 % white spirit. Long, oxidising		8–12 (resin)			Good colour retention and water resistance. Finishes for iron, metal signs, railway equipment, street cars, etc.
AROPLAZ 935 .	60% solids in white spirits, as 935 above		8–12 (resin)			

AROPLAZ 940 .	50% solids in white spirit. Medium to long oil. Oxidising		6–10 (resin)		As 900 but slightly longer and lower viscosity. Slightly slower drying.
AROPLAZ 945 .	65% solids in xylol. Medium oil, semi-oxidising		4–7 (resin)		Lacquers with good durability and colour retention. Motor-car, refrigerator, wood and paper lacquers. Stoving finishes with U.F. resins.
AROPLAZ 950 .	70 % solids in toluol, medium to short oil, oxidising		4–7 (resin)	C.S. alcohol	N.C. lacquers and spirit varnishes.
AROPLAZ 950 .	70 % solids in Hi-Flash; as above		4–7 (resin)	As 950 above	
AROPLAZ 955 .	50 % solids in 12·5 % white spirit and 37·5 % xylol. Short oil. Oxidising		6–8 (resin)		Hard, durable, colour retentive, stoving finishes. Aluminium paints motor-car primers and enamels, etc.
AROPLAZ 960 .	60 % solids in white spirit. Long oil. Oxidising		4–8 (resin)		Air-drying enamels, including whites.
AROPLAZ 980 .	50 % solids in white spirit, as 940 but slightly lower viscosity		6–10 (resin)		
AROPLAZ 1015 .	Pure alkyd, oil free	66°–70° C.	44–50		Cellulose acetate lacquers to give gloss and adhesion with good colour retention.
AROPLAZ 1031 .	50 % solids in white spirit. Short oil, phenol modified, oxidising		8–12 (resin)		Quick drying, water resisting durable finishes. Not for whites. Primers and surfacers. Special wood lacquers.
AROPLAZ 1031 .	50% solids in toluol as 1031 above		8–12 (resin)		As 1031 above.
AROPLAZ 1041 .	60% solids in toluol. Short modified, oxidising, non-phenolic		35–45 (resin)		For cheap, hard lacquers of good adhesion and colour retention. Wood lacquers.

CONSTANTS OF SYNTHETIC RESINS: ALKYD RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
AROPLAZ 1065	50% solids in 25% Solvesso 2 and 25 % Shell TS-28. Medium oil, oxidising		10–15 (resin)			Hard stoving finishes with good colour retention. Finishes for motor-cars, bicycles, trucks, etc.
AROPLAZ 1070	75% solids in white spirit. Very long oil, oxidising		6–10 (resin)			Blending with shorter alkyds to improve brushing and flow. House paints, etc.
AROPLAZ 1075 .	50% solids in white spirit. Long oil, oxidising		6–12 (resin)			Good durable and drying finishes. Paints for aluminium, farm equipment, etc.
AROPLAZ 1080 .	60% solids in white spirit. Long oil, oxidising		5–7 (resin)			Good brushing and flow. Slower drying than 900, 940 or 1115. For aluminium, freight cars, structural and woodsign primers and paints.
AROPLAZ 1085 .	50% solids in white spirit. Medium oil, oxidising		4–7 (resin)			More difficult to brush than 960 or 1120 but harder and quicker drying and better gloss retention. Stoving finishes with good colour retention.
AROPLAZ 1085 .	65% solids in white spirit, as 1085 above		4–7 (resin)			As 1085 above.
AROPLAZ 1090 .	55% solids in 40·5% white spirit, and 4·5% high flash naphtha. Short oil, modified, non-phenolic, oxidising		12–20 (resin)			Quick drying, water resistant durable finishes with good colour retention. Suitable for whites. Motor-car enamels, metal finishes, roller coating and toy finishes.

AROPLAZ 1095 .	50 % solids in white spirit. Medium oil, oxidising		3–7 (resin)			As 1085 but slightly better water resistance. Decorative enamels and finishes for farm machinery, petrol pumps, refrigerators, etc.
AROPLAZ 1100 .	50% solids in xylol. Short oil, oxidising		26–36 (resin)			Quick air-drying and stoving finishes with good water resistance and durability for clears and colours.
AROPLAZ 1105 .	70 % solids in white spirit. Long oil, oxidising		2–6 (resin)			As 1080 but slightly lower viscosity. Fortified for oil paints and for finishes and primers for aluminium, freight cars and structures.
AROPLAZ 1110 .	50 % solids in toluol. Medium-short, non-oxidising		16–26 (resin)			As 945 but slightly greater viscosity and adhesion. Feeds with zinc oxide. For automobile, refrigerator, and wood lacquers.
AROPLAZ 1115 .	50 % solids in white spirit. Medium oil, oxidising; between 900 and 940		5–8 (resin)			Slightly slower drying than 900, but better through dry than 900 or 940. For petrol pumps, metal primers, roller coating enamels, and automobiles.
AROPLAZ 1115 .	55 % solids in white spirit		5–8 (resin)			As above.
AROPLAZ 1120 .	60 % solids in white spirit. Medium long oil, oxidising		7–9 (resin)			Similar to 960 and 1085, but midway for brushing and sagging.
AROPLAZ 1125 .	50 % solids in white spirit. Medium short oil, oxidising		20–25 (resin)			Hard resin with fair durability, colour retention and drying time. For metal finishes.
AROPLAZ 1130 .	50 % solids in 12·5 % white spirit and 37·5 % xylol. Short oil, oxidising		4–6 (resin)			As 955 but better colour retention and through dry. Compatible with most ureas.
AROPLAZ 1130 .	60 % solids in xylol, as 1130 above		4–6 (resin)			As 1130 above.

CONSTANTS OF SYNTHETIC RESINS: ALKYD RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
AROPLAZ 1130	65 % solids in xylol, as 1130 above		4–6 (resin)			As 1130 above.
AROPLAZ 1140	70 % solids in white spirit. Very long oil, oxidising		6–10 (resin)			Good flow and brushing properties. Decorative finishes in white or colours.
AROPLAZ 1195	50 % solids in xylol. Short oil, phenol modified, oxidising		8–16 (resin)			Quick setting and drying primers with good adhesion and toughness. For N.A. Spec. P.27b-2 for zinc chromate primer.
AROPLAZ 1230	50 % solids in xylol. Medium short oil, oxidising		7–10 (resin)			Air drying and low stoving spraying enamels. Quick drying and good colour retention. Compatible with ureas.
AROPLAZ 1240	70 % solids in white spirit		6–10 (resin)			Similar to 1140. Bureau of Ships Ad. Interim Spec. 52-R-13.
AROPLAZ 1280	50 % solids in high solvency naphtha		10–15 (resin)			Hard, tough, glossy air-drying and stoving enamels and primers.
AROPLAZ 1295	60 % solids in xylol		22–28 (resin)			Spraying, air-drying and low stoving finishes. For use in F-5 of N.A. Spec. P-27b-2 for zinc chromate primer.
AROPLAZ 1305	Highly modified, oil extended		10–20			Best cooked further with dehydrated castor oil. Whites and colours for general inside and outside use.
AROPLAZ 1320	55 % solids in white spirit		5–8 (resin)			Similar to 1115. For H.Q.D. Spec. ES680. 1321 has higher viscosity than 1320.
AROPLAZ 1321	50 % solids in white spirit		5–8 (resin)			

Bakelite BR 14590	Carbic anhydride type. Oil reactive	Liquid	45–60		1·030	Rapid heat bodying with soft oils. Textile coatings, printing inks, overprint varnishes for paper and metal. Coatings for metal cap liners. Quick drying enamels.
Bakelite BR 13202	Carbic anhydride type. Resin modified	115°–137° C.	<15		1·13	Good colour retention; quick drying with soft oils. Enamels with good gloss retention.
Wresin 6 . .	Drying oil modified		5–10	C.S. hydrocarbons	1·08	Media for brushing decorative finishes.
Wresin 7 . .	Drying oil modified		5–20	C.S. aromatic hydrocarbons		Media for coloured spraying finishes for stoving.
Wresin 8 . .	Drying oil modified		10–15	C.S. hydrocarbons	1·05	As Wresin 6 but less viscous.
Wresin 11 . .	Drying oil modified		15–20	C.S. aromatic hydrocarbons	0·97	Media for white spraying finishes for stoving.
Wresin 12 .	Non-drying oil modified		10–15	As 11		Plasticiser for nitrocellulose and urea formaldehyde resins
Wresin 13 .	Non-drying oil modified		15–20	C.S. 4 : 1 aromatic hydrocarbon : butanol		As 12 but shorter. Essentially for nitrocellulose.
Wresin 20 H.V. .	Drying oil modified		10–15	C.S. hydrocarbons	1·07	As 20 V. 8 but more viscous.
Wresin 20 V. 8 .	Drying oil modified		10–15	As 20 H.V.		Media of good water resistance and colour retention.
Wresin 25 .	Drying oil modified		5–10	As 20 H.V.	1·10	Quick drying media for industrial finishes, air-drying or stoving.
Rezyl 12 . .	Solid resin	63°–66° C.	21–27		1·20	Nitrocellulose clear and pigmented furniture lacquers. Resistant to rubbing oils. Durable.
Rezyl 12–5 .	50% soln. in xylol. (49% phthalic anhydride)		20–28			

CONSTANTS OF SYNTHETIC RESINS: ALKYD RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
REZYL 14 . .	Solid resin	61°–65° C.	26–34		1·33	Pale nitrocellulose lacquers for polished metals. Durable. Cellulose acetate and butyrate lacquers.
REZYL 19 . .	Solid resin	64°–67° C.	21–27		1·19	Clear, translucent and opaque lacquers for motor cars. Good colour retention and durability. Sanding sealers and furniture lacquers.
REZYL 22 . .	Solid resin	63°–66° C.	57–66		1·19	Clear and pigmented metal lacquers. Quick stoving enamels with urea formaldehyde resins.
REZYL 53 . . Soln. F.	80% soln. in toluol	Viscous liquid	19–23 (solid resin)		1·14 (solid resin)	Clear nitrocellulose lacquers for paper and furniture. White refrigerator lacquers. Grinding vehicle. Lacquer type printing inks.
REZYL 99–4 .	Saturated type alkyd, free from resin or phenol	55°–58° C.	4–8	C.S. aromatic hydrocarbons, lacquer solvents P.S. aliphatic hydrocarbons	1·17	Nitrocellulose lacquers. Clear and pigmented. Durable. Resistant to rain-spotting.
REZYL 99–5 . .	60% soln. in xylol. 42% phthalic anhydride		4–8	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons		Urea and melamine lacquers with good colour retention. Can be used with basic pigments.
REZYL 110 . . Soln. C.	70% soln. in xylol		49–57	C.S. aliphatic hydrocarbons S. drying oils	1·13 (solid resin)	Air-drying and low temperature stoving enamels and undercoats. Aluminium media. For mixing with linseed oil paints. Nitrocellulose lacquer primers and inks.

REZYL 113 . . Soln. G.	60% soln. in xylol		22–28 (solid resin)	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons	1·13 (solid resin)	Air-drying enamels for brushing or spraying. Chromate primers. Stoving primers and primer surfacers. Nitrocellulose lacquers for alcohol resistance and outside durability.
REZYL 114 . . Soln. J.	60% soln. in xylol		29–37 (solid resin)	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons	1·13 (solid resin)	Air-dry and low temperature stoving enamels and undercoats.
REZYL 330–5 .	50% soln. in xylol. 39% phthalic anhydride		6–10	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons	1·16	Air-drying and baking clear finishes and enamels in white and light tints. Good colour retention and durability. Nitrocellulose lacquers.
REZYL 387–2 .	50% soln. in hydrogenated naphtha. 41% phthalic anhydride		6–12 (solid resin)	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons	1·16 (solid resin)	As 330–5 but paler and less yellowing tendency. Less resistant to water and grease.
REZYL 387–4 .	60% soln. in toluol		6–12 (solid resin)	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons	1·16 (solid resin)	In spraying and dipping enamels for quicker set than 387–2. Nitrocellulose exterior lacquers.
REZYL 387–5 .	55% soln. in xylol. Oxidising. 41% phthalic anhydride		6–12	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons		N.C. lacquers and urea and melamine formaldehyde finishes.
REZYL 412–1 .	50% soln. in mineral spirits. 31% phthalic anhydride		3–7 (solid resin)	C.S. aliphatic hydrocarbons	1·10 (solid resin)	Air-drying and baking finishes. Durable with good colour retention.
REZYL 418–1 .	60% soln. in white spirit. 31% phthalic anhydride		3–7	C.S. aliphatic hydrocarbons		Army-Navy Aeronautical Spec. AN-TT-V-116, amend. 2. Glyceryl phthalate spar varnish.

CONSTANTS OF SYNTHETIC RESINS: ALKYD RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
REZYL 420–5	60% soln. in xylol		4–8 (solid resin)	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons	1·13 (solid resin)	High temperature stoving enamels alone and with urea formaldehyde resin. Heat resistant enamels.
REZYL 727–5	50% soln. in xylol. 36% phthalic anhydride		12–20	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons		Quick drying zinc chromate primers permitting rosin; ammunition finishes.
REZYL 728–5	50% soln. in xylol. 35% phthalic anhydride		12–20	As 727–5		Congo modified vehicle for A.N.A. Spec. AN-TT-P-656b, amend. 1. Primer 52P68.
REZYL 729–5	50% soln. in xylol. 39% phthalic anhydride		10–16	As 727–5		Ammunition and camouflage finishes, allowing rosin. Fast drying enamels.
REZYL 731–6	55% soln. in high flash naphtha. No phthalic anhydride		10–20	As 727–5 but improved white spirit tolerance		Interior air-drying or stoving enamels, with or without urea or melamine resins.
REZYL 741–1	60% soln. in white spirit. 15–16% phthalic anhydride		5–10	C.S. white spirit		Semi-alkyd formulations.
REZYL 775–1	50% soln. in mineral spirits. Phenol modified alkyd. 17% phthalic anhydride		17–24 (solid resin)	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons	1·06 (solid resin)	Air-drying and baking coloured enamels, undercoatings, etc.
REZYL 775–4	70% soln. in toluol Phenol modified alkyd		17–24 (solid resin)	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons	1·06 (solid resin)	As above but for fast setting. Nitrocellulose lacquer for alcohol resistance. Used with chlorinated rubber.
REZYL 784–1	60% soln. in white spirit. No phthalic anhydride		10–18	C.S. white spirit		White brushing enamels.

REZYL 807 . .	Oxidising alkyd, free from rosin or phenol. 30% phthalic anhydride	3–7	S. aliphatic hydrocarbons	1·14	Air-drying and baking finishes.
REZYL 819–1 .	50% soln. in white spirit. 31·5% phthalic anhydride	6–10	C.S. white spirit		General purpose vehicles.
REZYL 822–1 .	70% soln. in white spirit. 23% phthalic anhydride	4–10	C.S. white spirit		Fast drying vehicle for U.S. Maritime Commission Spec. 52-MC-21.
REZYL 823–1 .	50% soln. in white spirit. 35% phthalic anhydride	6–10	C.S. white spirit		General purpose vehicle. Quick drying durable coloured enamels.
REZYL 824–1 .	50% soln. in white spirit. 31·5% phthalic anhydride	6–10	C.S. white spirit		Compatible with varnishes.
REZYL 829 . .	Pure resin	4–8	C.S. aliphatic hydrocarbons	1·08	Long oil glyptal. Aluminium media. Paints for smoke stacks, ironwork, etc. Baking primers. Shingle stains.
REZYL 863–1 .	70% soln. in white spirit. 27% phthalic anhydride	2–6	C.S. white spirit		Easy brushing paints. Emulsion paints. Suitable for use with basic pigments.
REZYL 869 . .	Pure resin	2–6	C.S. aliphatic hydrocarbons S. drying oils	1·08	Durable, easy working paints, varnishes and enamels. Grinding vehicle. Dries quicker and harder than 829.
REZYL 869–1 .	70% soln. in mineral spirits. 27% phthalic anhydride	2–6 (solid resin)	C.S. aliphatic hydrocarbons S. drying oils	1·08 (solid resin)	Durable, easy working paints, varnishes and enamels. Grinding vehicle. Dries quicker and harder than 829.
REZYL 871–1 .	70% soln. in white spirit. 24% phthalic anhydride	6–10	C.S. white spirit		Meets U.S. Navy Bureau of Ships Spec. 52R13.

CONSTANTS OF SYNTHETIC RESINS: ALKYD RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
REZYL 880–1	60% soln. in mineral spirits. Oxidising alkyd resin. 28% phthalic anhydride		4–6	C.S. aliphatic hydrocarbons P.S. drying oils		Non-yellowing decorative enamel. Nitrocellulose lacquers.
REZYL 1102 Soln. A.	40% soln. in xylol. 50% phthalic anhydride		53–61 (solid resin)	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons	1·21 (solid resin)	Quick stoving enamels at 180°–220° F. Nitrocellulose lacquers for durability.
REZYL 1103	Solid resin		28–33	C.S. aliphatic hydrocarbons P.S. drying oils	1·08	For use alone or with drying oils as paint media. Printing inks.
REZYL 7872–1	70% soln. in white spirit. 25% phthalic anhydride		6–10	C.S. white spirit		As 871–1. Exterior brushing enamels.
REZYL X-315	Solid resin 9% phthalic anhydride. Non-oxidising		13–19	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons		Flexible lacquers for textiles, paper, leather, wood and metal. Plasticiser for urea and melamine resins.
Beckolin 27 (Light) (R.C.I.)	Synthetic oil	Liquid	6–10	C.S. varnishes, white spirit P.S. oils	1·036	For improving durability, resistance to chalking, and drying of paints and enamels. Excellent grinding medium.
BECKOLIN 17. (Dark) (R.C.I.)	Synthetic oil	Liquid	10–14	As for Beckolin 27	0·981	Similar in many respects to No. 27, but cheaper and darker. Not always interchangeable.
Beckosol 1 (R.C.I.)	Phenol modified alkyd, oil extended. 50% solids in mineral spirits	Liquid	8–12	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons and drying oils	0·912	Medium, long oil. Water resistant durable finishes. Air-drying brushing and spraying finishes. Oil and grease resistant. Stoving enamels.

BECKOSOL 2 (R.C.I.)	Phenol modified alkyd, oil extended	8–12	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons and drying oils	0·911–0·913	As 1 but darker in colour
BECKOSOL 1303 (R.C.I.)	Phenol modified alkyd. 50 % solids in xylol	13–18	C.S. Aromatic hydrocarbons P.S. aliphatic hydrocarbons I.S. drying oils	0·990–0·994	Short oil length. A dark grade of 1320 with higher viscosity. Chassis blacks, fender enamels, quick drying primers and undercoatings.
BECKOSOL 1304 (R.C.I.)	Phenol modified alkyd. 50 % solids in xylol	13–18	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons I.S. drying oils	0·990–0·994	Short oil length. As 1320 but darker. To be used in place of 1320 to reduce cost.
BECKOSOL 1306 (R.C.I.)	Pure alkyd resin without phenol or resin modifying agents. 50 % solids in No. 2 hydrogenated naphtha	3–6	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons I.S. drying oils	0·976–0·980	Medium oil length.
BECKOSOL 1307 Light (R.C.I.)	Pure alkyd resin without phenol or resin modifying agents	3–6	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons I.S. drying oils	0·986–0·990	Medium oil length. 50% solids in xylol. Dipping enamels. White spraying stoving enamels. Air-drying durable varnishes.
BECKOSOL 1307 ex. Light (R.C.I.)	Pure alkyd resin without phenol or resin modifying agents	3–6	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons I.S. drying oils	0·986–0·990	As 1307 Light.
BECKOSOL 1308 (R.C.I.)	Pure alkyd non-drying	3–13	C.S. aromatic hydrocarbons Almost I.S. aliphatic hydrocarbons	0·992–0·996	Medium oil length. 50 % solids in toluol. A resin-plasticiser for nitrocellulose.
BECKOSOL 1308X (R.C.I.)	As 1308 but in xylol				
BECKOSOL 1308 DP (R.C.I.)	As 1308 but in dibutyl phthalate				

CONSTANTS OF SYNTHETIC RESINS: ALKYD RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
BECKOSOL 1313 Light (R.C.I.)	Pure alkyd resin without phenol or resin modifying agents. 45% solids in No. 2 hydrogenated naphtha		3–6	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons I.S. drying oils	0·973–0·977	Medium/short oil length. For durable air-drying and baking finishes. Primers, surfacers and finishes for motor cars. Good colour retention against light and dark and low stoving temperatures.
BECKOSOL 1313 ex. Light (R.C.I.)	As 1313 Light		3–6	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons I.S. drying oils	0·973–0·977	As 1313 Light.
BECKOSOL 1316 (R.C.I.)	Phenol modified alkyd, oil extended		8–12	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons and drying oils	0·952–0·956	As No. 1 but 50% soln. in toluol. For cellulose lacquers. Alkali, alcohol and water resistant.
BECKOSOL 1318 (R.C.I.)	Description as 1307 but 80% soln. in mineral spirits		6–10	C.S. aliphatic hydrocarbons P.S. drying oils	0·986–0·990	Extra long oil. Air-drying exterior paints and enamels. Wall finishes, metal primers structural steel coatings, oil fillers, putty glazes.
BECKOSOL 1319 (R.C.I.)	Non-phenolic alkyd		8–12	C.S. aromatic hydrocarbons and most oils P.S. aliphatic hydrocarbons	0·938–0·942	67% soln. in mineral spirits. Long oil length. Flat and gloss wall paints. Tin printing finishes. Flexible baking finishes. Little tendency to yellowing.
BECKOSOL 1320 (R.C.I.)	Short oil modified alkyd containing phenol 50% solids 50% xylol		13–18	C.S. aromatic hydrocarbons P.S. white spirit	0·990–0·994	Rapid air-drying and baking finishes.

BECKOSOL 1323 (R.C.I.)	Non-drying pure alkyd. 50 % solids in toluol		3–6	C.S. aromatic hydrocarbons Almost I.S. aliphatic hydrocarbons	0·995–0·999	Short oil length. Non-drying. For exterior non-yellowing white lacquers.
BECKOSOL 1323 ex. Light (R.C.I.)	As 1323 but lighter		3–6	C.S. aromatic hydrocarbons Almost I.S. aliphatic hydrocarbons	0·995–0·999	As 1323.
BECKOSOL 1324 (R.C.I.)	Non-drying pure alkyd. 80% soln. in toluol		3–6	C.S. aromatic hydrocarbons Almost I.S. aliphatic hydrocarbons	1·000–1·004	Extra long oil length. A resin plasticiser. For clear and pigmented lacquers for wood, metal, composition board, paper, cloth, rubber, leather, and all flexible surfaces.
BECKOSOL 1325 (R.C.I.)	Phenol modified alkyd		13–18	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons I.S. drying oils	0·989–0·993	Exactly as 1320 but 50 % soln. in No. 2 hydrogenated naphtha.
BECKOSOL 1326 (R.C.I.)	Phenol modified alkyd, oil extended		8–12	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons and drying oils	0·941–0·946	As No. 1 but 50% soln. in No. 2 hydrogenated naphtha. For spraying finishes. Quicker dust-free dry than No. 1.
BECKOSOL 1328 (R.C.I.)	Phenol modified alkyd		13–18	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons I.S. drying oils	0·989–0·993	50 % in No. 2 hydrogenated naphtha. Short oil length. Chassis blacks, fender enamels, low-priced undercoats and synthetic enamels for brushing and spraying. Air-drying or stoving finishes.
BECKOSOL 1329 (R.C.I.)	Phenol modified alkyd		6–10	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons I.S. drying oils	0·936–0·940	50 % soln. in No. 2 hydrogenated naphtha. Short oil length. Toy enamels and cheap black enamels. Air-drying and stoving.

CONSTANTS OF SYNTHETIC RESINS: ALKYD RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
BECKOSOL 1331 (R.C.I.)	Drying type pure alkyd. 50% soln. in mineral spirits		3–6	C.S. *aliphatic* hydrocarbons P.S. drying oils	0·920–0·924	Long oil length. Non-yellowing vehicles. White air-drying and baking enamels. Grinding pastes.
BECKOSOL 1332 (R.C.I.)	As 1331 but darker		3–6	C.S. aliphatic hydrocarbons P.S. drying oils	0·920–0·924	As 1331.
BECKOSOL 1333 (R.C.I.)	Drying type pure alkyd. 45 % soln. in high flash naphtha		8–12	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons	0·960–0·964	Medium oil length. Rapid through drying and excellent hardness are its chief properties. Durable air-drying and baking finishes.
Beckosol 1313 (B.K.C.)	Pure drying oil type. Linseed. 40·5% fatty acid. 45 % solids in xylol.		4–8	C.S. aromatic hydrocarbons. Good white spirit tolerance	0·990	Low bake enamels and air-drying industrial finishes.
BECKOSOL 2911 (B.K.C.)	Pure drying oil type. Dehydrated castor. 45·2 % fatty acid. 50 % solids in xylol		9–13	As above but better white spirit tolerance	0·995	High bake stoving finishes. Good colour retention and water resistance. Compatible with N.C.—half hour synthetic and reflow enamels
BECKOSOL 1333 (B.K.C.)	Pure drying oil type. Linseed-wood oil. 48·4 % fatty acid. 50 % solids in xylol		12–16	C.S. aromatic hydrocarbons. Fair white spirit tolerance	0·993	Industrial air-drying and stoving finishes, primers, etc.
BECKOSOL 9610 (B.K.C.)	Pure drying oil type. Linseed-dehydrated castor 57·6 % fatty acid 50 % solids in white spirit		7–11	C.S. aliphatic hydrocarbons	0·920	Longer oil type than 2911. For air-drying brushing finishes. Non yellowing whites. Replaces 1331.

BECKOSOL 9670 (B.K.C.)	Pure drying oil type. Linseed-wood oil. 50 % solids in white spirit				Stoving finishes of good gloss, colour, flexibility and adhesion. Roller coating enamels.
BECKOSOL 2912 (B.K.C.)	Pure drying oil type. Dehydrated castor. 50 % solids in white spirit		6–10	C.S. aliphatic hydrocarbons	0·918	General purpose stoving and air-drying industrial finishes.
BECKOSOL 1441 (B.K.C.)	Pure drying oil type. Linseed 60·4 % fatty acid 50 % solids in white spirit		8–12	As 2912	0·925	The most universal alkyd in the range. Air-drying and stoving finishes. Rapid through drying—no after tack.
BECKOSOL 1430 (B.K.C.)	Pure drying oil type. Linseed-wood oil 64·4 % fatty acid 50 % solids in white spirit		8–12	As 2912	0·915	Modified with pure phenolic. Decorative and coach finishes. Excellent gloss, through-hardening, water resistance and exterior durability.
BECKOSOL 3157 (B.K.C.)	Pure drying oil type. Linseed 66·8 % fatty acid 75 % solids in white spirit		3–7	C.S. aliphatic hydrocarbons	0·983	Properties comparable with Beckosol 1430, exterior durability slightly better, but drying properties not quite as good. Outstanding for ships topside paints.
BECKOSOL 18 (B.K.C.)	Pure drying oil type. Linseed-wood oil 66·6 % fatty acid 100 % solids		8–12	As 3157	1·05 0	Compatible with ethyl cellulose. Printing ink media.
BECKOLIN (B.K.C.)	Pure drying oil type. Linseed 71·5 % fatty acid 100 % solids		8–12	As 3157	1·030	Universal grinding medium. Excellent compatibility with varnishes, oils and nitrocellulose. Can replace stand oil in varnishes, giving improved durability, drying time and water resistance.

CONSTANTS OF SYNTHETIC RESINS: ALKYD RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
BECKOSOL 4401 (B.K.C.)	Pure drying oil type. Linseed 73·3 % fatty acid 75 % solids in white spirit		6–10	As 3157	0·963	Long oil maleic alkyd; dries similar to 3157, but softer film. Outstanding water resistance and compatibility.
BECKOLIN 403 (B.K.C.)	Pure drying oil type. Linseed 86·3 % fatty acids 100 % solids		8–12	As 3157	0·986	Similar to 4401 but longer oil length. Similar to Beckolin which it is likely to substitute.
BECKOSOL 3246 (B.K.C.)	Pure non-drying type 30 % fatty acid 50 % solids in toluol		3–7	C.S. aromatic hydrocarbons I.S. aliphatic hydrocarbons	1·023	For N.C. lacquers. Replaces Beckosol 1323. Excellent colour retention, toughness, water resistance and polishing properties. Car lacquers. Plasticiser for U.F. resins.
BECKOSOL 1308 (B.K.C.)	Pure non-drying type 42·5 % fatty acid 50% solids in xylol		11–15	As 3246	0·997	Plasticiser for U.F. and N.C. Gives softer films than Beckosol 3246. Little after yellowing. Ideal where maximum flexibility required.
BECKOSOL 24 (B.K.C.)	Pure non-drying type 78 % fatty acid 100 % solids		5	I.S. aliphatic hydrocarbons		Very long oil plasticising resin for N.C. Excellent colour and maximum flexibility at low temperatures.
BECKOSOL 59 (B.K.C.)	Pure non-drying type 100 % solids		47–53	I.S. aliphatic hydrocarbons	1·023	Non-phthalic alkyds, specially developed for plasticising U.F. resins. Excellent adhesion, mar-proofness, and colour retention.
BECKOSOL 416 (B.K.C.)	Pure non-drying type 100 % solids		57–63	As 59	1·007	

BECKOSOL 1320 . (B.K.C.)	Rosin modified, linseed oil alkyd 42·5 % fatty acid 50 % solids in xylol		13–17	C.S. aromatic hydrocarbons Fair white spirit tolerance ance	1·007	Rapid air-drying and low bake industrial finishes. Metal primers, and surfacers, grain fillers.
BECKOSOL 1 . (B.K.C.)	Phenol modified, linseed-wood oil alkyd 72 % fatty acid 50 % solids in white spirit		6–10		0·916	Very hard air-drying and stoving industrial finishes, particularly automobile primers and surfacers, petrol resisting finishes, and excellent water resistance.
BECKOSOL P239 . (B.K.C.)	Phenol modified, linseed oil alkyd 66·3 % fatty acid 50 % solids in white spirit		6–10		0·917	Similar properties to Beckosol 1.
Synolac SB. 102 .	Unmodified		92–110	C.S. esters, ketones, alcohols		Binding agent for mica. Nitrocellulose lacquers. Rubber-stereo printing inks. Spirit varnishes.
SYNOLAC SB. 121 .	Modified with natural resin. 57% fatty acid		18–22	C.S. benzol-alcohol, esters S.H. linseed oil (250° C.)		Nitrocellulose lacquers. Sanding sealers. Cheap enamels. Photogravure inks.
SYNOLAC SB. 144.	Drying oil (linolenic free), 30% fatty acid	Tough solid	37–42	C.S. turpentine, naphtha, esters, higher alcohols P.S. white spirit		Non-yellowing, air-drying and stoving varnishes and white enamels. Nitrocellulose lacquers, sanding sealers. Short oil varnishes.
SYNOLAC SB. 144X	As 144 but 40% xylol					
SYNOLAC SB. 145.	Drying oil. 48% fatty acid	Viscous liquid	10–12	C.S. white spirit, naphtha, esters, turpentine		Non-yellowing stoving finishes.
SYNOLAC SB. 147.	Linseed oil. Fatty acid 60%		10–12	C.S. white spirit, naphtha, esters, turpentine		Paints, varnishes, printing inks. Anti-corrosive primers.
SYNOLAC SB. 148.	Linseed-tung oil. 48% fatty acid	Viscous liquid	12–15	C.S. white spirit, naphtha, esters, turpentine		Exterior enamels. Stoving finishes and primers. Nitrocellulose lacquers.
SYNOLAC SB. 148X	As 148. 34% xylol					

CONSTANTS OF SYNTHETIC RESINS: ALKYD RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
SYNOLAC SB. 149.	Linseed oil. 48% fatty acid	Viscous liquid	12–14	C.S. white spirit, naphtha, esters, turpentine		Hard enamels, industrial finishes, stoving primers. Nitrocellulose.
SYNOLAC SB. 149X	As 149 but 34% xylol					
SYNOLAC SB. 150.	Linseed oil. 70% fatty acid		8–12	C.S. all common paint solvents		General paints, varnishes and printing inks.
SYNOLAC SB. 164.	Non-drying oil. 30% fatty acid		50–57	C.S. aromatic hydrocarbons, alcohols, esters, ketones		Nitrocellulose lacquers.
SYNOLAC SB. 164X	As 164 but 50% xylol					
SYNOLAC SB. 166.	Non-drying oil. 48% fatty acids	Viscous liquid	10–12	C.S. hydrocarbons, esters higher alcohols, ketones		Plasticising resin for use with SB. 144. Solvent plasticiser for nitrocellulose.
SYNOLAC SB. 166X	As 166 but 30% xylol					
SYNOLAC SB. 542.	Linseed oil. 75% fatty acid		10–12	C.S. all common paint solvents		Paint and enamels with good colour retention.
SYNOLAC SB. 546.	Drying oil (linolenic acid free). 36% fatty acid	Viscous liquid	25–30	C.S. white spirit, naphtha, esters, turpentine		Hard drying paints and varnishes of good water resistance and colour retention. Non-yellowing white stoving enamels.
SYNOLAC SB. 546X	As 546 but 20% xylol					
SYNOLAC SB. 565.	Non-drying oil. 44% fatty acid	Viscous liquid	20–25	C.S. aromatic hydrocarbons, higher alcohols, esters		Non-yellowing resin plasticiser for nitrocellulose lacquers and urea resins.
SYNOLAC SB. 565X	As 565 but 25% xylol					
SYNOLAC SB. 1442	Linseed oil and phenolic resin. 68% fatty acid		15–19	C.S. all common paint solvents		Rapid hardening and water resistant paints and enamels.

Synolac SB. 1442 W	As 1442 but 30% white spirit			
Falkyd A–2	60% soln. in hydrogenated naphtha. Air-drying	18–24	C.S. aromatic or hydrogenated hydrocarbons	Industrial stoving enamels
FALKYD A–3	50% soln. in white spirit. Air-drying	4–5	C.S. aromatic and aliphatic hydrocarbons	Durable automobile and general industrial finishes.
FALKYD A–4	50% soln. in white spirit. Air-drying	4–6	C.S. white spirit	Petrol resisting finishes, marine paints and general exterior use.
FALKYD A–5	85% soln. in white spirit. Air-drying	4–6	C.S. white spirit	Air-drying brushing enamels, paint fortifier, general grinding medium.
FALKYD A–5D	70% soln. in white spirit. Air-drying	4–6	C.S. white spirit	Very good compatibility with most varnish constituents.
FALKYD B–2	60% soln. in toluol. Non-yellowing	6–8	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons	Non-yellowing stoving enamels.
FALKYD B2S	50% soln. in hydrogenated naphtha. Non-yellowing	6–8	As B2	As B2.
FALKYD B3	50% soln. in white spirit. Non-yellowing	3–4	C.S. white spirit	Non-yellowing white enamels, gloss paints, etc.
FALKYD B41	65% soln. in white spirit. Non-yellowing	4–5	C.S. white spirit	As B3 but slightly slower dry.
FALKYD B5	85% soln. in white spirit. Non-yellowing	4–6	C.S. white spirit	To increase durability, washability and drying of house paints.
FALKYD C3	50% soln. in hydrogenated naphtha. Fish oil type	4–5	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons	Aluminium paints.
FALKYD C5	70% soln. in high solvency white spirit. Fish oil type	4–5	C.S. white spirit	An economical general purpose alkyd.
FALKYD C5D	70% soln. in hydrogenated naphtha. Fish oil type	4–6	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons	Heat resistant aluminium paints. Heavier bodied than C–5.

CONSTANTS OF SYNTHETIC RESINS: ALKYD RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
FALKYD L42.	60% soln. in hydrogenated naphtha. Non-drying		6–8			For lacquers and urea resins.
FALKYD L-4-X	50% soln. in xylol. Non-drying		9–11			For non-yellowing stoving lacquers and urea resins.
FALKYD B4Q	80% soln. in white spirit. Natural resin modified		4–6	C.S. white spirit		Interior house paints and enamels.
Falkote 240	Rosin modified	110°–115° C. S.Pt. R. and B.	30–36	C.S. white spirit C.S.H. drying oils		N.C. lacquers. Hardener for oils, alkyds, etc. Good gloss, colour retention and alkali resistance.
FALKOTE 285	Rosin modified	136°–140° C. S.Pt. R. and B.	30–36	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons		As 240.
FALKOTE 315	Rosin modified	148°–152° C. S.Pt. R. and B.	30–36	As 285		As 240
Petrex 1	Modified alkyd	105°–110° C. (S.Pt.)	8–10	C.S. hydrocarbons, drying oils, esters I.S. alcohols	1·125	Varnishes, lacquers.
PETREX 2	Oxidising alkyd	Plastic	45	As 1	1·09	Air-drying and low temperature stoving finishes.
PETREX 3	Oxidising alkyd	Plastic	40	As 1	1·07	As 2.
PETREX 4	Oxidising alkyd	Plastic	25–30	As 1	1·08	Auto refinish enamels, house paints, exterior white enamels.
PETREX 5	Unmodified	95°–100° C. (S.Pt.)	35	C.S. aromatic hydrocarbons, esters I.S. aliphatic hydrocarbons, drying oils, alcohols	1·213	High temperature and thermoplastic lacquers.
PETREX 6	Unmodified. (In solution only)	Plastic	35	As 5	1·19	Soft lacquer resin.

PETREX 7 . .	Unmodified. (In solution only)	Plastic	35	As 5	1·19	As 6
PETREX 21 . .	Unmodified	65°–75° C. (S.Pt.)	38	As 5	1·195	Heat sealing adhesives.
PETREX 22 .	Unmodified. (In solution only)	65° C. (S.Pt.)	38	As 5	1·200	Flexible non-tacky paper lacquers.
Duraplex A. 25	Drying. Oil content 50%		15–24	P.S. white spirit		Non-yellowing. 60% solids in xylol. Stoving primers. Clear bond coat in metal decoration. Low temperature melamine finishes.
DURAPLEX A. 27	Drying. Oil content 37%		3–5	P.S. white spirit		Non-yellowing. 60% solids in xylol. White stoving finishes with or without urea and melamine resins.
DURAPLEX C–45 .	Drying. Oil content 56%		3–9	C.S. white spirit		60% solids in white spirit. Air-drying enamels, maintenance paints and roller coating enamels.
DURAPLEX C–45HV	Drying. Oil content 53%		3–9	C.S. white spirit		60% solids in white spirit. As C 45 but quicker drying.
DURAPLEX C–45LV	Drying. Oil content 60%		15–25	C.S. white spirit		Processing with resins and oils.
DURAPLEX C–46 .	Drying. Oil content 52%		3–8	C.S. white spirit		50% solids in white spirit. Transparent finishes, roller. coating and air-drying enamels.
DURAPLEX C–48 .	Drying. Oil content 63%		3–5	C.S. white spirit		Non-yellowing. 60% solids in white spirit. White enamels.
DURAPLEX C–49	Drying. Oil content 54%		1–4	C.S. white spirit		Non-yellowing. 60% solids in white spirit. Transparent and metal finishes. Roller coating finishes.
DURAPLEX C–50	Drying. Oil content 69%		9–15	C.S. white spirit		Non-yellowing. 60% solids in white spirit. For blending with other vehicles in metal decorating and metal furniture finishes.

CONSTANTS OF SYNTHETIC RESINS: ALKYD RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
DURAPLEX C-50LV	Drying. Oil content 70%		15–25	C.S. white spirit		Non-yellowing. Processing with resins and oils.
DURAPLEX D-63	Drying. Oil content 65%		3·5–7	C.S. white spirit		Non-yellowing. 70% solids in white spirit. Mill whites, marine paints, trim colours, house paint reinforcement.
DURAPLEX E-71	Drying. Oil content 77%		15–25	C.S. white spirit		Typographic inks, overprint varnishes, house paint reinforcement.
DURAPLEX E 73	Drying. Oil content 75%		10–20	C.S. white spirit		As E 71
DURAPLEX ND-75	Non-drying. Oil tent 42%		3–9	I.S. white spirit		60% solids in xylol. Non-yellowing. Plasticiser for N.C., urea and melamine lacquers.
DURAPLEX ND-77	Non-drying. Oil content 40%		3·5–6	I.S. white spirit		60% solids in xylol. Non-yellowing. As ND 75. Better colour retention at normal and high temperatures.
Amberlac 80 MT	Drying. Resin modified. Oil content 37%		10–20	P.S. white spirit		50% solids in white spirit. Air-drying and quick force dry finishes.
AMBERLAC 80 X	As 80 MT	14–28		P.S. white spirit		70% solids in xylol. Primers and surfacers for wood and metal. Quick drying enamels. Metal coatings.
Amberlac 85 X	As 80 MT		14–28	P.S. white spirit		70% solids in xylol. Primers and surfacers for wood and metal, especially with zinc chromate.

Paraplex G–20 .			6–12	C.S. *aromatic* hydrocarbons, esters, higher alcohols, glycol ethers	1·01	60% solids in butyl acetate. For N.C.
PARAPLEX RG.–2			13–21		0·96	60% solids in xylol. For N.C.
PARAPLEX RG–4			9–21	C.S. aromatic hydrocarbons, esters, glycol ethers, turpentine, tetralin. P.S. white spirit.	0·94	60% solids in xylol. For N.C.
PARAPLEX RG–7			21–29	As G–20	0·98	60% solids in xylol. For N.C.
PARAPLEX AL–16			< 14	P.S. hydrocarbons and alcohol C.S. esters	1·05	70% solids in xylol. For N.C. For use as plasticiser with Amberol 801.
PARAPLEX AL–19			< 13	C.S. hydrocarbons and esters	1·01	70% solids in xyol. For N.C.
PARAPLEX AL–111			< 15	C.S. aromatic and hydrogenated hydrocarbons, esters P.S. white spirit	0·96	Solid resin. For N.C.
PARAPLEX 5 B .			36–46	As G 20	0·98	80% solids in xylol. For N.C.

CONSTANTS OF SYNTHETIC RESINS: CASHEW NUTSHELL LIQUID RESINS

Epok H512/60 .	Cashew nutshell liquid-aldehyde resin. 60 % solids in Pool Rubber solvent		*p*H 7·5–8·5	C.S. aliphatic, aromatic and chlorinated hydrocarbons. *Drying oils*	0·890	Insulating varnishes. Chemically resistant varnishes. Solvent resistant finishes.
EPOK H514/60 .	As 512 but 60 % solids in white spirit		*p*H 6·5–7·5	As H512	0·900	As H512.
EPOK H515/70 .	As 512 but 70 % solids in xylol		*p*H 6·5–7·5	As H512	0·950	As H512.
EPOK H516/60 .	As 512 but 60 % solids in Pool Rubber solvent		*p*H 6·5–7·5	As H512	0·890	As H512.

CONSTANTS OF SYNTHETIC RESINS: *COUMARONE RESINS*

Nevillite 1, 2 and 3 . .	Cyclo-paraffin or naphthalene polymer	145°–155° C.	0·4 approx.	C.S. aromatic, aliphatic and chlorinated hydrocarbons, esters, ketones, vegetable oils I.S. alcohols	1·05	Durable varnishes, chemical resistant varnishes. Concrete enamel media; moisture, brine and alcohol resistant varnishes.

CONSTANTS OF SYNTHETIC RESINS: COUMARONE RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
Nevillac 10 .	Phenol modified coumarone-indene	5°–15° C.		C.S. castor oil, fatty acids, alcohol, aromatic hydrocarbons, ketones, esters, ethers, varnish oils, chlorinated hydrocarbons I.S. polyhydric alcohols	1·10–1·12	Ant-fouling paints, printing inks, adhesives, nitrocellulose lacquers.
NEVILLAC Soft .	Phenol modified coumarone-indene	65°–75° C.			1·10–1·12	Ant-fouling paints, printing inks, adhesives, nitrocellulose lacquers.
NEVILLAC Hard .	Phenol modified coumarone-indene	85°–95° C.			1·10–1·12	
***Nevindene* RESINS** R. 1, 3, 5, and 6	*Coumarone-indene*	Highest of R Series				Rapid drying varnishes, printing inks, aluminium media, insulating varnishes.
465 RESIN . .	Coumarone-indene polymers with metallic soaps of a monobasic alicyclic acid	110°–125° C.	0	C.S. aromatic hydrocarbons, esters, ethers, ketones, chlorinated hydrocarbons, drying oils, turpentine P.S. mineral spirits, alcohols I.S. polyalcohols	1·20	For tung oil varnishes. Water, acid and alkali resistant varnishes.
Neville RESIN R. 7 . .	Coumarone-indene resin	110°–150° C.		C.S. esters, aromatic and aliphatic hydrocarbons, chlorinated hydrocarbons I.S. alcohols, glycols, methyl cellosolve		Hard varnishes free from odour.
NEVILLE RESIN R. 8 . .	Coumarone-indene resin	Less than 110° C.				
NEVILLE RESIN R. 9, 10, 11, 12	Coumarone-indene resins. Grades vary only in colour	127°–142° C.			1·15	For general varnishes and adhesives. Chemical and alcohol resistant varnishes, brine and heat resisting varnishes, insulating varnishes, odourless and tasteless varnishes, spar varnishes, durable varnishes.
NEVILLE RESIN R 13, 14, 15, 16	Coumarone-indene resins	95°–127° C.			1·15	

NEVILLE RESIN R. 17	Coumarone-indene resin	80°–95° C.	C.S. esters, aromatic and aliphatic hydrocarbons, chlorinated hydrocarbons I.S. alcohols, glycols, methyl cellosolve	1·08 approx.	Adhesives, waterproofing and plastic compositions. R. 21 also used for fly-papers.	
NEVILLE RESIN R. 19	Coumarone-indene resin	55°–80° C.		1·08		
NEVILLE RESIN R. 21	Coumarone-indene resin	45°–55° C.		approx. 1·08		
NEVILLE RESIN R. 22	Coumarone-indene resin	10°–45° C.		approx. 1·08		
NEVILLE RESIN R. 26, 27, 28, 29	Coumarone-indene resins. Grades vary only in colour	10°–95° C.		approx. 1·08 approx.		
NEVILLE RESIN R. 33	Coumarone-indene resin	20°–35° C.	C.S. esters, aromatic and aliphatic hydrocarbons, chlorinated hydrocarbons I.S. alcohols, gycols, methyl Cellosolve		For dark media and lower priced varnishes and coatings.	
NEVILLE RESIN R. 34	Coumarone-indene resin	35°–45° C.				
NEVILLE RESIN R. 35	Coumarone-indene resin	45°–75° C.				
NEVILLE RESIN R. 36	Coumarone-indene resin	75°–100° C.				
NEVILLE RESIN R. 37, 37A	Coumarone-indene resins	100°–125° C.				
NEVILLE RESIN R. 38	Coumarone-indene resin	125°–140° C.				
NEVILLE RESIN G	Coumarone-indene resin	110°–125° C.			Metallic paint media, alkali resisting varnishes, concrete and traffic paint media, and diluent for phenolic resins.	
Paradene No. 1	Coumarone-indene resin	75°–99° C.	C.S. aromatic hydrocarbons		Resin is brown to black in colour. Metallic paint media, adhesives, insulating varnishes, fillers, water and chemical resistant varnishes, concrete sealers, chassis blacks.	
PARADENE No. 2	Coumarone-indene resin	100°–124° C.	C.S. aromatic hydrocarbons			
Nuba 1	Coumarone-indene resin, a resinous pitch	80°–95° C.	P.S. aromatic hydrocarbons P.S.H. aliphatic hydrocarbons		Alkali resistant compositions, insulating compositions.	

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
NUBA 2 . .	Coumarone-indene resin, a resinous pitch	100°–125° C.		P.S. aromatic hydrocarbons P.S.H. aliphatic hydrocarbons		Alkali resistant compositions, insulating compositions.
NUBA 3 . .	Coumarone-indene resin, a resinous pitch	135°–150° C.		P.S. aromatic hydrocarbons P.S.H. aliphatic hydrocarbons		
X. 1 RESINOUS OIL . .	Coumarone-indene resin	Viscous oil			1·05–1·15	As plasticiser for chlorinated rubber and in aluminium media.
Phenester .	Coumarone-indene resin containing uncondensed phenolic bodies	95°–105° C.		C.S. aromatic hydrocarbons, ketones, esters, ethers, varnish oils, chlorinated hydrocarbons I.S. alcohols, polyhydric alcohols	1·12	Varnishes containing tung oil.
Epok C. 46 .	Coumarone-indene	100°–105° C.	0–2	C.S. aliphatic hydrocarbons, drying oils		Heat-resisting paints. Insulating varnishes, plaster primers.
EPOK C. 50 .	Coumarone-indene	65°–85° C.	0–2	As C. 46		Softer variety of C. 46.
EPOK C. 60 .	Coumarone-indene	Soft resin	0–2	As C. 46		Plasticiser for chlorinated rubber. Cable lacquers, primers. Rubber compounds.
R.I. 8026 . .		60°–65° C.		C.S. benzol, toluol, solvent naphtha, turpentine, acetates, drying oils I.S. alcohols	1·05–1·15	For aluminium media, anti-fouling, and road-marking media. Chemically resistant and insulating varnishes.
R.I. 8027 . .		75°–85° C.			1·05–1·15	
R.I. 8028 . .		95°–105° C.			1·05–1·15	
R.I. 8029 . .		115°–125° C.			1·05–1·15	

R.I. . . .		135° C.			1·05–1·15	For aluminium media, anti-fouling, and road-marking media. Chemically resistant and insulating varnishes.
R.I. . . .		180° C.			1·05–1·15	

CONSTANTS OF SYNTHETIC RESINS: MALEIC ANHYDRIDE RESINS

Crestanol SB. 522		100°–107° C.	10–15	C.S. drying oils and common solvents	1·06	Cheap non-yellowing varnishes. Miscible with nitrocellulose.
CRESTANOL SB. 523		124°–132° C.	30–35	C.S. drying oils I.S. white spirit	1·06	For short and medium oil length media for whites.
CRESTANOL SB. 524		118°–127° C.	18–23	C.S. white spirit + alcohol I.S. white spirit	1·08	As SB. 526 but harder and better gloss
CRESTANOL SB. 526		126°–136° C.	20–25	C.S. white spirit + alcohol I.S. white spirit	1·08	Hard, glossy, durable, brushing and spraying media for whites. Miscible with nitrocellulose and alkyds.
Paranol LB. 1 .		113°–118° C.	15–20	P.S. mineral spirits C.S. aromatic hydrocarbons I.S. alcohol	1·16	Stoving finishes. Nitrocellulose lacquers.
PARANOL LB. 5 .		113°–118° C.	35–40	C.S. aromatic hydrocarbons P.S. mineral spirits I.S. alcohol	1·11	Tin-decorating varnishes, white enamel media, sealers. Nitrocellulose lacquers.
PARANOL LB. 89 .		104°–110° C.	12–14	C.S. mineral spirits, aromatic hydrocarbons I.S. alcohol	1·11	As LB. I.
PARANOL LN. 100		127°–132° C.	23–35	P.S. mineral spirits C.S. aromatic hydrocarbons I.S. alcohol	1·11	Nitrocellulose lacquers, sealers, tin-decorating varnishes, printing ink media.
PARANOL 1639 .		132°–138° C.	25–30	C.S. aromatic hydrocarbons I.S. alcohol and mineral spirits	1·10	Sealers, printing ink media, lithographic varnishes and white stoving enamel media.

CONSTANTS OF SYNTHETIC RESINS: MALEIC ANHYDRIDE RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
PARANOL 1650		127°–132° C.	15–20	C.S. aromatic hydrocarbons P.S. mineral spirits I.S. alcohol	1·10	Nitrocellulose lacquers, white enamel media, tin-decorating varnishes, printing and lithographic varnishes, sealers, rubbing lacquers.
Albertol 177C	Non-phenolic	88°–98° C.	15	C.S. drying oils	1·11	
ALBERTOL 201C	Non-phenolic	140° C.	25	C.S. aromatic hydrocarbons, turpentine, esters, ketones P.S. white spirit		As Bedesol 72
Bedesol 55		150°–160°C.	35–41	C.S. aromatic hydrocarbons, turpentine		Very hard resin, particularly suitable for varnishes with excellent build, e.g. overprinting varnishes.
BEDESOL 72		145° C.	28	C.S. aromatic hydrocarbons, turpentine, ester solvents, ketones P.S. white spirit		For pale varnishes and enamels. Tin-printing media. White indoor and outdoor enamels. Baking whites. Ships' paints. Nitrocellulose lacquers. Blending with alkyds.
BEDESOL A72		145° C.	28	As 72		Darker grade of Bedesol 72.
Wresin 3	Maleic anhydride modified	140° C.	25	C.S. aromatic hydrocarbons		Media for white paints and enamels with good colour retention. N.C. sanding sealer.
WRESIN 17	Maleic anhydride modified	130° C.	25	C.S. hydrocarbons		As Wresin 3 but softer. N.C. lacquers and enamels.
Beckacite 1110 (R.C.I.)	Non-phenolic	93°–102° C.	17–22	C.S. acetates, coal-tar solvents, turpentine, drying oils P.S. mineral oils I.S. alcohols	1·14 1·18	As 1111 but not so hard.

BECKACITE 1111 (R.C.I.)	Non-phenolic	110°–120° C.	22–28	C.S. acetates, coal-tar solvents, turpentine C.S.H. drying oils I.S. alcohols and mineral spirits	1·14 1·18	Sanding sealers and cellulose lacquers. Short and medium oil length varnishes of good colour retention. Media for whites, air dry and stoving. Difficult to obtain gas-proofness with this resin.
BECKACITE 1114 (R.C.I.)	Non-phenolic	93°–102° C.	17–22	As 1110	1·14 1·18	As 1110 but colour.
BECKACITE K. 100 P. (B.K.C.)		116°–122° C. B. & R.	15–20			Hard gloss paints with excellent initial colour and colour retention, particularly suitable for whites. Beckacite K. 100 P. suitable for cold cutting and low temperature cooking. Compatible with nitrocellulose, and suitable for wood and general industrial cellulose lacquers. The harder resin has excellent polishing and sanding properties.
BECKACITE K. 125 P. (B.K.C.)		126°–132° C. B. & R.	15–20			
BECKACITE 6763 (B.K.C.)		112°–118° C.	15–20			New resin of same type as above. Compatible with N.C. and drying oils. Uses as K.100 P. and K. 125 P.
Erinite 200		86°–95° C.	12	C.S. turpentine, white spirit, naphtha		See Albertol 177C. See Albertol 201C. Printing inks, sanding sealers, nitrocellulose lacquers. Stoving enamels.
ERINITE 201		102°–109° C.	13	C.S. turpentine, white spirit, naphtha		
ERINITE 202		121°–127° C.	25	C.S. turpentine, white spirit, naphtha		
Glycodiene NAH				C.S. drying oils after heat treatment. Varnishes require some aromatics in thinners		
GLYCODIENE NAC				As NAH but more soluble in aliphatic hydrocarbons		In nitrocellulose lacquers.

CONSTANTS OF SYNTHETIC RESINS: MALEIC ANHYDRIDE RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
GLYCODIENE NAW	Not so hard as NAH or NAC			C.S. drying oils and white spirit		For light fast varnishes and nitrocellulose lacquers.
Epok 400M	Maleic-rosin-glycerine	115°–120° C.	9–12	C.S. N.C. solvents C.S.H. drying oils P.S. aliphatic hydrocarbons		Harder than 422M. Rapid solvent release and heat-processed oil varnishes.
EPOK 422M	Maleic-rosin-glycerine	105°–115° C.	9–12	C.S. drying oils, N.C. solvents. P.S. aliphatic hydrocarbons		Harder than 438M.
EPOK 438M	Maleic-rosin-glycerine	100°–105° C.	9–12	C.S. aliphatic hydrocarbons, drying oils, nitrocellulose solvents.		Pale non-yellowing oil varnishes. N.C. lacquers.
Amberol 800	Rosin modified	122°–126° C. B. & R.	15–30	C.S. hydrogenated naphthas, turpentine, aromatic hydrocarbons	1·13	Non-yellowing. Stoving finishes, tin decorating finishes, for modifying alkyd resins, and for nitrocellulose lacquers.
AMBEROL 801	Rosin modified	142°–149° C. B. & R.	25–40	P.S. white spirit acetone I.S. alcohol	1·13	
AMBEROL 801P	Rosin modified	134°–142° C. B. & R.	25–40	C.S.H. drying oils	1·13	Amberol 808 is specially designed for soft oils.
AMBEROL 806 P	Rosin modified	145°–150° C. B. & R.	25–40		1·13	
AMBEROL 808	Rosin modified	146°–152° C. B. & R.	< 20		1·11	
Amberlac D96		78°–82° C. (S. pt.)	30–50	As Amberol 800		For N.C. lacquers. More durable, better gloss retention and less tendency to cold checking than above Amberols.
AMBERLAC B–94		42°–48° C. (S. pt.)	22–32		1·05	80% solids in xylol. As D96
Texyn T20	Drying oil modified		25–30	C.S. white spirit and common varnish solvents, drying oils		Durable air-drying and stoving finishes with good colour retention.

TEXYN T5 . .	Plasticising resin		20–25	C.S. lacquer solvents except industrial alcohol		N.C. lacquers of good durability and colour retention.
Featalak M171 .	Rosin modified	104°–108° C.	18–25	C.S. cyclic hydrocarbons, esters, drying oils		
Krumbhaar 414		150° C.				Air-drying and stoving white undercoats and enamels.
KRUMBHAAR 404		130°–135° C.	25–30			N.C. lacquers, sanding sealers, interior and exterior lacquers and enamels. Metal finishes.

CONSTANTS OF SYNTHETIC RESINS: MELAMINE-FORMALDEHYDE RESINS

Beetle RESIN 52 . B.E. 615	55% solids 45% butanol		2–3	C.S. aromatic hydrocarbons or alcohols	1·05	Rapid hardening and low stoving finishes. Hard, moisture resistant, white enamels.
BEETLE 230–8 .	Melamine-urea 50% resin 27·5% butanol 22·5% xylol		2–4	Fair tolerance to white spirit		Very quick hardening at 200° F.
BEETLE RESIN 4000 B.E. 618	50% solids 50% *thinners*		5–6	C.S. mixture of alcohols and aromatic hydrocarbons	1·00	Low stoving, flexible, clear and white finishes. Cellulose lacquers.
Super-Beckamine 3500 . . (R.C.I.)	Melamine formaldehyde condensation product, 50% resin, 15% xylol, 35% butyl alcohol		less than 1·0	C.S. alcohols, esters, aromatic hydrocarbons, ketones, turpentine, Cellosolve, chlorinated hydrocarbons P.S. aliphatic hydrocarbons	1·02–1·03	High temperature refrigerator enamels. Hard low temperature enamels. Hard, tough, rapid drying primers.
Uformite MM 55	Melamine-butanol 50% solids in xylol-butanol (1 : 3)		0–1	C.S. alcohols, esters, ketones, cellosolve and cellosolve acetate	1·00	Quick drying stoving finishes. Good heat, solvent and chemical resistant lacquers.
UFORMITE MU–56	Urea modified melamine		0–1		1·00	50% solids in xylol-butanol (1 : 1). As MM 55.

CONSTANTS OF SYNTHETIC RESINS: MELAMINE-FORMALDEHYDE RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
Melmac 245–8 .	50% resin 25% butanol 25% xylol		< 1	P.S. white spirit		Quick drying stoving finishes, for range 200°–325° F. Good colour retention at 425° F.
MELMAC 560–8 .	Alkyd modified melamine 55% resin 22·5% butanol 22·5% xylol		2–5	Fair tolerance to white spirit		Good gloss and colour retention at high temperatures. For stoves, radiators, etc.
MELMAC 583–9 .	Alkyd modified melamine 50% resin 20% pine oil 15% butanol 15% white spirit		1–3	Good tolerance to white spirit		Roller coating and dipping stoving enamels.
MELMAC 599–8 .	Alkyd modified melamine 50% resin 25% butanol 25% xylol		5–8	Fair tolerance to white spirit		Very quick hardening at 200° F.

CONSTANTS OF SYNTHETIC RESINS: MISCELLANEOUS RESINS

Albertol 218V .	Thermosetting			C.S. benzole		Lacquers for aluminium, light metals, nickel, copper and chromium. Good adhesion and heat resistance.
ALBERTOL 503V .						
KM RESIN Special . .	Ester type of copal character. Free from phenols or aldehydes	105°–110° C.	20	C.S. mineral spirits, turpentine, aromatic hydrocarbons, esters, drying oils P.S. alcohols		Excellent light fastness. Very slight yellowing up to 80°–90° C.
KM RESIN Palest . .	Ester type of copal character. Free from phenols or aldehydes	110°–115° C.	20–25	As KM Special		Durable water resisting varnishes.
KM RESIN Extra . .	Ester type of copal character. Free from phenols or aldehydes	135°–145° C.	20–25	As KM Special		

Durez 333 . .	Thermosetting resin			C.S. hexone 80%, Cellosolve 20%; alcohols, esters I.S. drying oils, petroleum and aromatic hydrocarbons		In lacquers for metal containers. Resistant to alkali and solvents, including acetone.
Resin MS. 2 .	Pure cyclic ketone resin	85°–95° C. (B. & R.)	0·0	C.S. aromatic and higher aliphatic hydrocarbons, acetates, butyl alcohol, chlorinated hydrocarbons P.S. methyl and ethyl alcohols I.S. hydroxy esters, ethers, ketones		Nitrocellulose lacquers. Miscible with chlorinated rubber and alkyds. Increases gloss, body and hardness of alkyds. Increases speed of dry of alkyds when stoved. Pale, durable oil varnishes, luminous and metallic paint media.
Velsicol AF–3 .	Polymerised hydrocarbon resin of petroleum origin	62°–85° C.	5	C.S. aliphatic and aromatic hydrocarbons, turps, drying oils P.S. alcohol, acetone	1·020–1·070	Acid and solvent resistant finishes.
Resin 1A† . .	Contains 25% rubber derivatives			C.S. mineral spirit Miscible with drying oils		Exceptional flexibility.
Resin R8‡ . .		101°–113° C.	8			Similar to ester gum but harder. Nitrocellulose lacquers and bituminous compositions.
AW. 2 Resin .		75°–90° C.	0·0	C.S. mineral spirits, drying oils, esters, aromatic hydrocarbons P.S. alcohols		Non-yellowing. Very pale. Chemical resistant, durable varnishes. Particularly suitable for white enamel media.
Aroclor 1262 .	Chlorinated diphenyl	35°–38° C. (pour pt.)		C.S. most common organic solvents, and drying oils	1·646–1·653	In fireproof materials, electrical lacquers, adhesives, and for water and moisture-proof impregnating compositions. Stable to caustic soda. Non-corrosive to mild steel.

† Wilfrid Smith Ltd.

‡ Taylor Bros. & Cox (Beck Koller Ltd.).

CONSTANTS OF SYNTHETIC RESINS: MISCELLANEOUS RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
AROCLOR 1269 .	Chlorinated diphenyl	Hard opaque solid		C.S. most common organic solvents, and drying oils	1·870–1·876	As 1262.
AROCLOR 2565 .	Chlorinated diphenyl	Soft. pt. 68°–72° C.		C.S. most common organic solvents, and drying oils	1·723–1·740	As 1262.
AROCLOR 4465 .	Chlorinated diphenyl	Soft. pt. 60°–66° C.		C.S. most common organic solvents, and drying oils	1·712–1·723	As 1262.
Clophen A. 60 .		Viscous liquid. B.pt. 200°–250° C./12 mm. Setting pt. 20° C.		C.S. aromatic hydrocarbons, butanol, esters. I.S. water P.S. ethyl and isopropyl alcohol	1·60	Alkali and acid resistant finishes. Non-inflammability. Nitrocellulose.
Hercolyn . .	Hydrogenated methyl abietate	B.pt. 365°–370° C.	2–8	C.S. esters, alcohols except methyl alcohol, ketones and aliphatic and aromatic hydrocarbons	1·025–1·035	Resin plasticiser for nitrocellulose. Furniture lacquers. Plasticiser for chlorinated rubber. Adhesives. Transparent paper lacquers.
Resilin 2 and 2A	Petroleum resins		0·0	Generally very soluble		Alkali resistant finishes. Produces "slip" in varnish films. Improves durability. Prevents skinning and precipitation of driers. Adhesives, paper varnishes, putty.
Amberol 925 .	Fortified rosin ester	122°–130° C. B. & R.	12–20	C.S. white spirit, hydrogenated naphthas, turpentine, aromatic hydrocarbons	1·10	Air-drying and stoving finishes.
AMBEROL 926 .	Fortified rosin ester	123°–132° C. B. & R.	12–18	P.S. acetone I.S. alcohol C.S.H. drying oils	1·10	
AMBEROL 750 .	Fortified rosin	155°–170° C. B. & R.	100–115	I.S. hydrocarbons and terpenes C.S. alcohol	1·20	Spirit varnish and wax emulsions.

Arochem 345 .	Modified condensate	110°–115° C. (Mercury)	5–10	C.S. aliphatic and aromatic hydrocarbons, and drying oils I.S. alcohol	1·10	Ester gum substitute with increased hardness, bodying and drying.
AROCHEM 505 .	Modified condensate	110°–115° C. (mercury)	10–15	As 345	1·10	For N.C. lacquers. Cheap varnishes of good colour retention and hardness.
AROCHEM 510 .	Modified condensate	135°–140° C. (mercury)	18–23	As 345	1·10	As 505 but better hardness and gloss. For NC. lacquers and varnishes. Stoving varnishes with good colour retention.
AROCHEM 515 .	Modified condensate	130°–135° C. (mercury)	15–25	As 345	1·10	As 1510 but slightly reduced melting point and hardness.
AROCHEM 520 .	Modified condensate	140°–145° C. (mercury)	25–35	C.S. aromatic hydrocarbons, and drying oils I.S. aliphatic hydrocarbons, alcohol	1·10	For very pale lacquers and for white air-drying and stoving finishes. For oil bodying.
AROCHEM 525 .	Modified condensate	140°–145° C. (mercury)	25–35	As 520	1·10	For short and medium oil length whites.
AROCHEM 530 .	Modified condensate	135°–140° C. (mercury)	25–35	As 520 but P.S. aliphatic hydrocarbons	1·10	Easier to handle then 525, and better alkali resistance. Good colour retention.
AROCHEM 535 .	Modified condensate	140°–145° C. (mercury)	25–30	As 520	1·12	For N.C. lacquers. Sanding sealers, furniture lacquers.
AROCHEM 540 .	Modified condensate	145°–150° C. (mercury)	20–25	As 530	1·12	Harder and faster drying lacquers then 535. Oil bodying.
AROCHEM 545 .	Modified condensate	140°–145° C. (mercury)	20–28	As 520	1·12	As 535, but slightly darker with better colour retention.
Teglac 164 .		140°–150° C.	35–45	C.S. xylol P.S. white spirit		Pale, high bodied varnishes with soft oils. White enamel media.
Phenac 604M .		146°–151° C.	16–20	C.S. xylol P.S. white spirit		Quick drying, water, alkali and abrasion resistant varnishes with soft oils.

CONSTANTS OF SYNTHETIC RESINS: MISCELLANEOUS RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
PHENAC 608		145°–150° C.	18–25	As 604M		Pale, high viscosity, quick drying varnishes with soft oils. Good colour retention.
PHENAC 615N		145°–152° C.	98–105	As 604M		Furniture rubbing varnishes.
Glyptolac	Alternative to oil modified alkyds		13	C.S. hydrocarbons, oils, esters, and ketones I.S. alcohols		Air-drying and stoving finishes. Good water resistance and durability. Tin-plate lacquers.
Parapen 4511	Pentaerythritol ester	110°–112° C. (capillary)	12–15	C.S. hydrocarbons, drying oils		Pale, quick drying varnishes, with good adhesion, hardness and water resistance.
PARAPEN 4513	Pentaerythritol ester	115°–120° C. (capillary)	12–18	As 4511		Pale, quick drying varnishes of good flexibility and hot water resistance.
PARAPEN 4515	Pentaerythritol ester	115° C. (capillary)	17–20	As 4511		
Krumbhaar 909	Synthetic copal	145° C.	18–25			Quick drying varnishes and enamels. Printing inks.
Wresin 35	General purpose	104° C.		C.S. white spirit, alcohols		Manila substitute, especially in road line paints.
WRESIN 90	General purpose			C.S. hydrocarbons		Road-line paint B.S. A.R.P. 38. Type 2.
Beckosol 792 (B.K.C.)	Phenolic type, containing linseed and dehydrated castor 50 % solids in white spirit		8–12	C.S. aliphatic hydrocarbons	0·900	Phenol formaldehyde media, suitable for air-drying and stoving industrial finishes. Primers for U.F. and cellulose finishes.
BECKOSOL 792 X. (B.K.C.)	Description as above 50 % solids in xylol		8–12	As 792	0·942	

BECKOSOL 805 (B.K.C.)	Cresylic type with dehydrated castor 70 % solids in white spirit		28–32	As 792	0·943	Cresol formaldehyde medium of longer oil length than Beckosol 792.
BECKOSOL 420 (B.K.C.)	Phenolic type with dehydrated castor 60 % solids in white spirit		5–9	As 792	0·910	Phenol formaldehyde medium of lower acid value but similar oil length to 805. Interior decorative finishes.

CONSTANTS OF SYNTHETIC RESINS: PHENOLIC RESINS (UNMODIFIED)

Amberol ST–137	Reactive	80°–90° C.† B. and R.	< 50	C.S. white spirit, turpentine, hydrogenated naphthas aromatic hydrocarbons, acetone	1·04	Durable tung oil varnishes with good alkali resistance.
AMBEROL ST–137X	Non-reactive	70°–95° C. B. and R.	< 50	P.S. alcohol C.S.H. drying oils	1·04	As ST–137, and in form of short tung oil varnish can be blended with alkyds to improve gloss and drying.
AMBEROL HH–1	Thermo-setting 70% soln. in toluol		< 7	C.S. aromatic and chlorinated hydrocarbons, ketones, esters, higher alcohols, turpentine, tetralin	0·97	Thermosetting resin for stoving finishes free of oil. Good hardness and solvent resistance.
Varcum 250	Oil soluble and oil reactive	100°–105° C.	30–40	C.S. alcohol, acetone, mineral spirits, ethyl acetate, and xylol C.S.H. wood oil, linseed and perilla oils	1·18	Chemical and water resistant varnishes. Durable exterior varnishes. For use with alkyds. When modified with ester gum for high gloss interior and exterior varnishes, medium-priced spar varnishes, floor varnishes, aluminium media.
VARCUM 250F.	Oil soluble and oil reactive. Quicker drying than Varcum 250	110°–115° C.	30–40	C.S. alcohol, acetone, ethyl acetate, xylol P.S. mineral spirits C.S.H. wood oil, linseed and perilla oils	1·18	Automobile finishes. Quick drying industrial finishes resistant to cleaning materials. Toy enamels. For use with alkyd resins and varnishes rich in perilla or fish oil.

† Since these may vary considerably during the heating process with oil, they are not necessarily of paramount importance.

CONSTANTS OF SYNTHETIC RESINS: PHENOLIC RESINS (UNMODIFIED)—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	*Recommended Uses.*
Varcum 700		65°–70° C.	25–35	C.S. alcohol, acetone, ethyl acetate, xylol P.S. mineral spirits C.S.H. wood oil, linseed and perilla oils	1·15	Aluminium media. Chemically resistant finishes. Specification finishes and dark industrial enamels. When modified with ester gum for baking enamels and floor paint media.
VARCUM 810	Heat reactive. Yields paler varnishes than 250 or 250 F.	78°–82° C.	20	C.S. acetone, xylol, mineral spirits, ethyl acetate I.S. alcohol P.S. soya bean oil C.S.H. wood oil, linseed and perilla oils	1·16–1·18	In quick setting varnishes. To improve water resistance of linseed oil or limed rosin varnishes. To accelerate the bodying of linseed oil. To improve the dry and hardness of ester gum varnishes.
VARCUM 965	Improvement on Varcum 365. Has higher m.pt., improved colour, gas-proofs wood oil easier. Yields harder films	70°–75° C. (R. and B.)	20–30	C.S. alcohol, acetone, ethyl acetate, xylol P.S. mineral spirits C.S.H. wood oil, linseed and perilla oils	1·20	Aluminium media. Dark coloured air-drying and baking enamels.
Bakelite XRB. 254	Non-heat reactive	91°–107° C.	85–105	C.S.H. drying oils	1·227	Yellows. Durable, rapid drying water resistant varnishes. Resistant to acids, alkalies, alcohols, and chemicals generally. Good electrical properties.
BAKELITE BR. 1329		141°–157° C.	55–65		1·10–1·15	Freedom from skinning. Aluminium media, anti-corrosive primers, media for chemically resistant paints and enamels.

BAKELITE XR. 3180		54°–66° C.	<20	C.S. aromatic hydrocarbons, ketones, esters P.S. alcohols, drying oils (hot) I.S. petroleum hydrocarbons, drying oils	1·30	For nitrocellulose lacquers. Resistant to weathering, oxidation, acids, oils and greases.
BAKELITE BR. 3360	Heat reactive	79°–96° C.			1·152–1·174	For reacting with ester gum. Slight yellowing tendency. Stoving varnishes. Spar varnishes and finishing varnishes. Good alkali resistance.
BAKELITE BR. 4036		85°–99° C.			1·04–1·07	Good light resistance. Freedom from skinning. Durable moisture and alkali proof varnishes.
BAKELITE R. 5503		Soft. pt. 115°–130° C.	46–68		1·145	Aluminium media, water resistant durable varnishes, anti-corrosive media and dark coloured paint media.
BAKELITE 10825/2	Heat reactive			C.S.H. drying oils		In combination with linseed oil as a substitute oil for tung oil in all types of varnish. Durable exterior varnishes with good water and chemical resistance, and colour retention.
BAKELITE R. 10840	Non-heat reactive	112°–125° C.	46–86	C.S.H. drying oils	1·17	Anti-corrosive and chemically resistant media and varnishes.
BAKELITE R 10857	Heat reactive			C.S.H. blown oils	1·145	Stoving varnishes and media. Insulating varnishes.
BAKELITE R11111	Non-heat reactive	100°–110° C.		C.S.H. drying oils		As for R 10840 but greater white spirit tolerance.
BAKELITE R11112	Non-heat reactive	95°–110° C.		C.S.H. drying oils		Durable moisture and alkali proof varnishes. Good light resistance and freedom from skinning.

CONSTANTS OF SYNTHETIC RESINS: PHENOLIC RESINS (UNMODIFIED)—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
Paradura AV .			35–40	C.S. aromatic hydrocarbons P.S. mineral spirits	1·10	Aluminium media, rust-proofing paint media, durable coloured paint media.
PARADURA 10P .			35–45	C.S. mineral spirits and aromatic hydrocarbons	1·05	Durable spar varnishes. Aluminium media. Floor varnishes. Coach and mixing varnishes.
PARADURA 367 .			45–55	C.S. mineral spirits and aromatic hydrocarbons	1·05	Durable spar varnishes. Floor varnishes. Coach finishes, exterior and interior varnishes, mixing varnishes.
PARADURA 540 .	Heat reactive				1·10	For hardening ester gum For quick drying, gas-proof alkali resistant and durable varnishes.
Lewisol 1501 .		145°–150° C.	80+	C.S. alcohols, esters C.S.H. drying oils I.S. aromatic, aliphatic hydrocarbons, turpentine		Yellows. Chemically resistant varnishes. Quick drying durable short varnishes.
LEWISOL 1701 .	Phenol formaldehyde type in alcohol. (70% solids)			Compatible with alcohols and ethers		Baking lacquers for metal. Chemical and solvent resistant. Film retains traces of phenolic odour.
LEWISOL 1702 .	As 1701			Compatible with alcohols and ethers		As 1701 but no phenolic odour. For tin-plate lacquers.
Glycophene N. Extra .		75°–85° C.		C.S. oils after treatment, aromatic and aliphatic hydrocarbons, and terpenes		Durable, water resistant and chemical resistant varnishes.
Erinite 10B .	Oil reactive	75°–80° C.		C.S. drying oil		For water and chemical resistant varnishes. Very little tendency to yellowing on exposure.

Super-Beckacite 1001 (R.C.I.)	Heat reactive. Oil reactive	50°–60° C.	60 initial 8–12 (after reaction)	C.S. acetates, coal-tar solvents, turpentine, drying oils P.S. mineral spirits I.S. alcohols	1·10–1·15	Durable exterior varnishes. Water and chemical resistant varnishes.
SUPER BECKACITE 1003 (R.C.I.)	Heat reactive. Oil reactive			As 1001	1·10–1·15	As 1001 but darker colour.
SUPER BECKACITE 2000 (R.C.I.)	Oil reactive	70°–80° C.	2–5	C.S. alcohols, acetates, coal-tar solvents, turpentine P.S. mineral spirits C.S.H. drying oils	1·05–1·09	Non-yellowing. Durable water resistant varnishes. Softer and slightly slower drying than 1001.
SUPER BECKACITE 2050 (R.C.I.)	Oil reactive	83°–90° C.	10–15	As 2000	1·05–1·09	As 2000 but darker in colour.
SUPER BECKACITE 2667 (R.C.I.)	Heat reactive. Oil reactive	92°–102° C.	55–60	As 2000	1·26–1·30	Hard, durable varnishes of good alkali and water resistance. Excellent gas-proofing and good anti-skinning properties. Yellows more and sets up more slowly than 1001, 1003, 2000 and 2050.
SUPER BECKACITE 3000 (R.C.I.)		135°–146° C.	85–105	C.S. alcohols, acetates, coal tar solvents I.S. mineral spirits and turpentine	1·17–1·23	For water, acid and alkali resisting varnishes. Rubbing varnishes. Gives good flexibility, tensile strength and durability with comparatively short oil varnishes.
SUPER BECKACITE 1001 (B.K.C.)	Resole. Oil reactive, heat hardening	80°–86° C. B. & R.				Long oil durable exterior varnishes, having good water resistance and gloss. For electrical insulation. Good colour retention.
SUPER BECKACITE 4000 (B.K.C.)	Novolak. Xylenol formaldehyde	87°–93° C. B. & R.				Durable finishes with good water, alkali, and soap resistance. Poor colour. Special cooking precautions necessary for best results.

CONSTANTS OF SYNTHETIC RESINS: PHENOLIC RESINS (UNMODIFIED)—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
SUPER BECKACITE 3554 (B.K.C.)	Novolak	72°–78° C. B. & R.				For short oil durable varnishes, with outstanding water, alkali, and soap resistance. Good solubility in mineral spirits and fairly good colour retention.
Crestin SB. 206	Slightly heat and oil reactive			C.S. drying oils and common solvents	1·10	Yellows. For dark anti-corrosive varnishes.
CRESTIN SB. 208	Heat reactive. Oil reactive with linseed or tung oil			C.S. drying oils and common solvents	1·10	Slight yellowing. High gloss, chemical, and water resisting varnishes.
Durez 202	Heat reactive. Oil reactive	74°–79·5° C.		C.S.H. drying oils With drying oils is soluble in mineral spirits	1·060	In hard, quick drying varnishes, e.g. rubbing varnishes, bar varnishes, floor varnishes, etc.
DUREZ 500	Thermoplastic. Oil soluble	60°–65° C. (capillary)	4–7	C.S. aromatic hydrocarbons, alcohols, ketones. I.S. aliphatic hydrocarbons, turpentine C.S.H. drying oils	1·140	
DUREZ 501	As 500	82°–90° C. (capillary)	23–25	C.S. aromatic and aliphatic hydrocarbons, ketones P.S. alcohols C.S.H. drying oils	1·085	
DUREZ 525	As 500	60°–65° C. (capillary)	15–20	As 500	1·164	
DUREZ 550	Heat reactive. Oil reactive	52° C.	0·5–1·0	C.S. alcohol, mineral spirits and drying oils	1·04	Non-yellowing interior and exterior enamels of high gloss.
DUREZ 570		60°–65° C.	30	C.S. drying oils, alcohols, lacquer solvents and mineral spirits	1·04	Chemical resistant finishes. Durable finishes. General purpose enamels, porch, deck, floor paints and varnishes.

DUREZ 11696 .	As 500	60°–65° C. (capillary)	9–12	As 500	1·142	
DUREZ 50733 .	As 500	96°–105° C. (capillary)	40–50	C.S. all hydrocarbons, alcohols, esters, ketones C.S.H. drying oils	1·047	
DUREZ 50950 .	As 500	112°–124° C. (capillary)	60–65	I.S. aliphatic and some aromatic hydrocarbons, and alcohol C.S.H. drying oils	1·048	
Arofene 700 .	Thermosetting	85°–100° C.	45–55	C.S. hydrocarbons and drying oils P.S. alcohol	1·1	Durable and chemical resistant varnishes. Minimum after-yellowing.
AROFENE 715 .	As 700 but less reactive	105°–115° C.	55–65	As 700	1·1	As 700 but darker in colour.
Krumbhaar 1010		115° C.		C.S. hydrocarbons		Chemical resistant finishes and boat varnishes.
Epok R. 7 . .	Xylenol formaldehyde	70°–75° C.		C.S. blown linseed oil		Insulating varnishes and compounds.
EPOK R. 713 .	Xylenol formaldehyde	Liquid		C.S. blown linseed oil		Thermohardening oil varnishes and lacquers.
EPOK R. 776 .	Heat and oil reactive	65°–75° C.		C.S. aromatic hydrocarbons, esters P.S. mineral spirits I.S. alcohols		Water and chemical resisting varnishes. Very little yellowing on exposure.
EPOK R. 780 .	Heat and oil reactive	65°–75° C.				As R. 776 but yellows on exposure.

CONSTANTS OF SYNTHETIC RESINS: PHENOLIC RESINS (MODIFIED)

Albertol 61L .	Oil soluble Albertol copal	93° C. (S. pt.) 103° C. (F. pt.) 140° C. (Fl. pt.)	150	C.S.H. drying oils P.S. alcohol C.S. acetates, aromatic hydrocarbons	1·089	Yellows. A hard Manila copal substitute.
ALBERTOL 62M .	Unesterified cresol-formaldehyde	155°–165° C.	105–115	C.S. aromatic hydrocarbons. P.S. white spirit		Very hard type resin for oil varnishes. General purpose varnish resin.

CONSTANTS OF SYNTHETIC RESINS: PHENOLIC RESINS (MODIFIED)—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
ALBERTOL 82G		80° C. (S. pt.) 90° C. (F. pt.) 120° C. (Fl. pt.)	82G/20 15–20 82G/10 5–10	C.S. mineral spirits, aromatic hydrocarbons, acetates, turps, and drying oils I.S. alcohols	1·087	For cellulose lacquers and fillers. Similar to 111L but better solubility in lacquer solvents, and better elasticity and adhesion in NC films.
ALBERTOL 88N	Oil soluble Albertol copal	95° C. (S. pt.) 105° C. (F. pt.) 140° C. (Fl. pt.)	50–55	C.S.H. drying oils C.S. acetates, aromatic hydrocarbons, turpentine I.S. alcohols P.S. mineral spirits	1·100	Yellows. Equal to 116Q in hardness, durability, drying. For floor and low-priced varnishes.
ALBERTOL 111L	Oil soluble Albertol copal	95° C. (S. pt.) 105° C. (F. pt.) 140° C. (Fl. pt.)	15–20	C.S. mineral spirits, varnish solvents, and drying oils, ether, acetates I.S. alcohol	1·091	Non-yellowing for use in oil varnishes and cellulose lacquers. Accelerates drying and useful in enamel media.
ALBERTOL 112M	Oil soluble Albertol copal	95° C. (S. pt.) 105° C. (F. pt.) 140° C. (Fl. pt.)	150	C.S. acetates, turpentine, drying oils P.S. alcohols, mineral spirits	1·087	As 61L but non-yellowing and paler. For pale spirit and acid resisting oil varnishes.
ALBERTOL 116Q	Oil soluble Albertol copal	95° C. (S. pt.) 105° C. (F. pt.) 140° C. (Fl. pt.)	15–20	C.S. acetates, turpentine, aromatic hydrocarbons P.S. mineral spirit C.S.H. drying oils	1·093	Similar to 111L but for cheap darker varnishes. For floor varnishes, oil glazes, gold stoving varnishes and printing inks. Yellows.
ALBERTOL 117R	Oil soluble Albertol copal	110° C. (S. pt.) 120° C. (F. pt.) 155° C. (Fl. pt.)	15–20	C.S. acetates, aromatic hydrocarbons C.S.H. turpentine, drying oils P.S. mineral spirits I.S. alcohols	1·100	Harder than 116Q. Yellows. For hard, quick drying durable finishes.
ALBERTOL 160L						Intermediate between 111L and 209L.

ALBERTOL 209L	Oil soluble Albertol copal	120° C. (S. pt.) 130° C. (F. pt.) 170° C. (Fl. pt.)	15–20	C.S.H. drying oils, turpentine C.S. acetates, aromatic hydrocarbons P.S. mineral spirits I.S. alcohols	1·097	For hard drying varnishes and media. Harder than 111L. Good chemical resistance and durability.
ALBERTOL 321L			<20			As 209L but harder.
ALBERTOL 326R	High phenolic type	55° C. (S. pt.) 65° C. (F. pt.) 100° C. (Fl. pt.)	75–85	I.S. petroleum hydrocarbons P.S. aromatic hydrocarbons	1·130	Gas-proof tung oil varnishes. Water and weather resistant boat varnishes. *Chemical resistant* varnishes.
ALBERTOL 118S	Oil soluble Albertol copal	120° C. (S. pt.) 130° C. (F. pt.) 170° C. (Fl. pt.)	15–20	C.S.H. drying oils, turpentine C.S. aromatic hydrocarbons, acetates P.S. mineral spirits I.S. alcohols	1·103	A hard resin similar to 209L. but tendency to yellow. Suitable for insulating varnishes and wire enamel media.
Bedesol 66	Esterified phenol-formaldehyde	136°–146° C.	11–16	C.S. aromatic hydrocarbons, turpentine. P.S. white spirit		General purpose varnish resin.
BEDESOL A. 66	Esterified phenol-formaldehyde	136°–146° C.	11–16	As 66		Darker grade of Bedesol 66.
Arochem 50		130°–135° C.	10–15	C.S. hydrocarbons and drying oils I.S. alcohol	1·1	General utility varnishes and enamels. Fair colour retention.
AROCHEM 55		140°–145° C.	13–18	As 50	1·1	As 50 but harder, better colour retention, alkali resistance and bodying properties.
AROCHEM 60		155°–165° C.	12–17	C.S. aromatic hydrocarbons and drying oils. P.S. aliphatic hydrocarbons I.S. alcohol	1·1	For bodying oils. Overprint varnishes.
AROCHEM 65		160°–170° C.	25–30	As 60	1·1	Hard pale varnishes. Good colour retention. Rubbing and overprint varnishes.
AROCHEM 75		165°–175° C.	23–28	As 60	1·1	As 65 but slightly harder and quicker bodying.

CONSTANTS OF SYNTHETIC RESINS: PHENOLIC RESINS (MODIFIED)—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
AROCHEM 80		135°–145° C.	12–18	C.S. hydrocarbons and drying oils I.S. alcohol	1·1	Four-hour enamel media. Good colour retention.
AROCHEM 85		150°–155° C.	12–18	As 80	1·1	As 80 but harder and quicker drying.
AROCHEM 90		130°–135° C.	10–15	As 80	1·1	General utility varnishes and enamels. Colour retention inferior to 80 and 85.
AROCHEM 95		145°–150° C.	10–15	As 80	1·1	As 90 but harder and quicker drying.
AROCHEM 100		125°–130° C.	10–15	C.S. hydrocarbons and drying oils I.S. alcohol	1·1	Not quite as hard as 90 but in same general class.
AROCHEM 110		115°–125° C.	10–15	As 100	1·1	Not quite as hard as 100 otherwise interchangeable.
AROCHEM 115		140°–145° C.	15–20	As 100	1·13	Quick drying, durable, alkali resistant varnishes with good colour retention. Stoving white enamel media.
AROCHEM 120		140°–145° C.	12–18	As 100	1·12	Quick drying, hard, alkali resisting varnishes. Floor, deck and porch finishes. For soft oils.
AROCHEM 125		140°–145° C.	20–25	C.S. aromatic hydrocarbons and drying oils P.S. aliphatic hydrocarbons I.S. alcohol	1·12	As 120 but better colour retention.
AROCHEM 130	Modified phenolic congo	140°–150° C.	10–20	As 125	1·1	Rubbing varnishes, spar varnishes and coloured enamels.
AROCHEM 260		150°–160° C.	12–18	As 125	1·1	Quick bodying with all oils.
AROCHEM 335		145°–160° C.	12–18	As 125	1·1	As 260 but better colour retention.

AROCHEM 365 .		140°–155° C.	12–18	C.S. hydrocarbons and drying oils I.S. alcohol	1·12	As 120 but colour retention.
AROCHEM 400 .		145°–155° C.	12–18	As 365	1·1	As 260 but slower bodying and drying. Superior alkali and water resistance.
Bakelite 302 .	Oil modified phenolic resin	Viscous liquid	34 approx.	C.S. aromatic hydrocarbons C.S.H. drying oils	1·043	Nitro cellulose lacquers, baking enamels, dipping enamels, asphaltum compositions, finishing varnishes.
BAKELITE 2175 .	Heat reactive	Viscous liquid	34	C.S.H. drying oils	1·063	As 302 but darker in colour and more reactive. Clear and pigmented baking finishes, glossy black enamels, and clear and pigmented heat resisting enamels.
BAKELITE BR. 2963		130°–150° C.		C.S.H. drying oils	1·112	Quick drying linseed oil paints and enamels. Good colour retention.
BAKELITE Z.3962/2	Resin-oil dispersion			C.S. aromatic hydrocarbons	1·02	Quick setting, anti-corrosive, primers for galvanised iron, aluminium alloy and other ferrous and non-ferrous metals.
BAKELITE Z–11120	As above			As above	1·02	As Z. 3962/2.
BAKELITE Z. 11170	As above			As above	1·02	As Z. 3962/2.
BAKELITE Z. 11096	As above			As above	0·915	Quick setting anti-corrosive primers.
BAKELITE Z. 11172	As above			As above	0·93	As Z. 11096.
BAKELITE PRIMER BASE Z. 5585 .	Resin dispersion in oil			C.S. aromatic hydrocarbons P.S. naphtha and turpentine	1·01 (solids 50–55%)	Especially for aluminium and aluminium alloy primers. More flexible, with better adhesion than 3962.
BAKELITE PRIMER BASE Z. 8989/1	Resin dispersion in oil			C.S. aromatic hydrocarbons P.S. naphtha and turpentine	0·9 (solids 30%)	As 3962 but especially for wood primers, fillers or sealers, where nitrocellulose is to be applied.

CONSTANTS OF SYNTHETIC RESINS: PHENOLIC RESINS (MODIFIED)—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
BAKELITE 10824 .		110°–115° C.	45–60		1·114	Cheap, quick drying interior and exterior varnishes and enamels.
Wresin 1 . .	Cresol formaldehyde. Contains glycerol	130° C.	25	C.S. aliphatic hydrocarbons		Media for general purpose paints and varnishes.
WRESIN 2 . .	As 1 but glycerol free	130° C.	130	As 1		As 1 but not with basic pigments.
WRESIN 4 . .	Modified cresol formaldehyde	140° C.	130	As 1		Printing inks. As 2 but harder and less soluble in bodied oils.
WRESIN 5 . .	Modified phenol formaldehyde	140° C.	15–20	C.S. aliphatic hydrocarbons		Quick drying water resisting varnishes.
WRESIN 9 . .	Modified cresol formaldehyde	150° C.	25	C.S. aromatic hydrocarbons		Media for quick drying ammunition paints to C.S. 1973 B.
WRESIN 32 .	Modified cresol formaldehyde	140°–150° C.	100	C.S. aliphatic hydrocarbons		As a congo copal substitute (non-maturing)
WRESIN 58 .	Modified cresol formaldehyde	105° C.	140	C.S. white spirit. Methanol		Road line paints.
WRESIN 58XH .	Modified cresol formaldehyde	115° C.	130	As 58		Harder than 58.
Paranol Hard .	Oil soluble modified phenol formaldehyde	121°–127° C.	12–16	C.S. mineral spirits, aromatic hydrocarbons I.S. alcohol	1·10	Grinding media, quick drying varnishes and enamels, baking varnishes and enamels.
PARANOL Ex. Hard . .	Oil soluble modified phenol formaldehyde	135°–141° C.	12–16	As Paranol Hard	1·09	Floor varnishes. Hard stoving varnishes and enamels.
PARANOL 25 light	Designed for use with soft oils	140°–146° C.	15–20	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons I.S. alcohol	1·14	Good water and alkali resistance but slightly slower drying than 1855.

PARANOL 54E .	High condensation content	160°–166° C.	15–20	Sol. mineral spirits C.S. aromatic hydrocarbons I.S. alcohol	1·09	Rubbing varnishes, floor varnishes, air-drying and stoving enamels.
PARANOL 105 .		113°–118° C.	12–15	C.S. coal-tar solvents P.S. mineral spirits I.S. alcohol	1·10	Grinding media, quick drying varnishes and enamels.
PARANOL 200 .	High condensation content	141°–146° C.	30–40	C.S. coal-tar solvents P.S. mineral spirits I.S. alcohol	1·09	Gas-proof, pale wood oil varnishes with good colour retention, alkali resistance and durability. Quick drying varnishes, white enamel media, rubbing varnishes, non-penetrating overprint varnishes, printing ink media, porch and deck enamels, and for bodying oils.
PARANOL Hard 500	Oil soluble modified phenol formaldehyde, but higher condensation content than standard Paranols	118°–124° C.	18–20	As Paranol Hard	1·08	Long gas-proof wood oil varnishes, with pale colour, good colour retention both on exposure and on stoving, and good alkali resistance. Grinding media.
PARANOL Ex. Hard No. 500 . .		132°–138° C.	18–20	C.S. mineral spirits, aromatic hydrocarbons I.S. alcohol	1·10	Pale varnishes and enamel media of good colour retention.
PARANOL 800 .		135°–141° C.	12–15	P.S. mineral spirits C.S. aromatic hydrocarbons I.S. alcohol	1·08	Non-penetrating primer and enamel media, printing ink media, overprint varnishes, linoleum varnishes.
PARANOL 850 .		135°–141° C.	95–100	C.S. aromatic hydrocarbons I.S. mineral spirits and alcohol	1·09	Rubbing varnishes, primer and surfacer media, quick drying stoving media.
PARANOL 1600 .		118°–124° C.	15–18	C.S. mineral spirits, aromatic hydrocarbons I.S. alcohol	1·08	Grinding media, mixing varnishes, pale, quick drying varnishes and media of good colour retention.

CONSTANTS OF SYNTHETIC RESINS: PHENOLIC RESINS (MODIFIED)—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
PARANOL 1700 .		129°–135° C.	12–15	As 1600	1·08	Pale varnishes and media of good colour retention. Alkali resistant finishes.
PARANOL 1750 .	Designed for use with soft oils	137°–142° C.	15–20	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons I.S. alcohol	1·09	For water and alkali resisting varnishes. Slower drying than 25 light.
PARANOL 1855 .	Designed for use with soft oils	140°–146° C.	15–20	C.S. aromatic hydrocarbons P.S. aliphatic hydrocarbons I.S. alcohol	1·14	A resin for rapid drying finishes with fair water and alkali resistance.
Epok R. 18 .	High phenolic content. Cresol formaldehyde in combination with monoglycerides of tung oil	40°–42° C.	60	C.S. drying oils	1·110	Durable, glossy, waterproof varnishes. Good colour retention and freedom from skinning. Marine varnishes, acid and alkali resistant varnishes and media. Low temperature stoving media. Insulating varnishes.
EPOK R. 22† .	As R. 18 but a lower percentage of monoglycerides of tung oil	64°–68° C.	30	C.S. drying oils	1·105	Durable, glossy, waterproof varnishes. Good colour retention and freedom from skinning. Exterior varnishes and media. Marine enamels and paint media. Stoving media and lacquers for tin-plate.
EPOK R. 33 .	Modified phenolic resin made from cresol formaldehyde and monoglycerides of tung oil	70°–73° C.	10	C.S. naphtha, xylol, butyl acetate, drying oils I.S. alcohol	1·09	Durable, glossy, waterproof varnish. Good colour retention and freedom from skinning. Coach varnishes, enamel and hard gloss media, nitrocellulose lacquers.

EPOK 52P . .	Phenolic-rosin-glycerine	104°–110° C.	16–20	C.S. mineral spirits, esters, oils. I.S. alcohols		Pale, quick-drying varnishes.
EPOK 78P . .	Phenolic-rosin-glycerine	125°–130° C.	16–20	C.S. aromatic hydrocarbons, esters C.S.H. drying oils P.S. white spirit I.S. alcohol		Hard four-hour varnishes, good chemical resistance and durability.
EPOK 137K .	Phenolic-rosin-glycerine	105°–110° C.	15–20	C.S. aromatics, esters, hot oils P.S. mineral siprits		As 52P but darker.
EPOK 148K .	Phenolic-rosin-glycerine	120°–127° C.	15–20			Hard variety of 137K. Quick air-drying finishes, printing inks, linoleum and stoving finishes.
Krumbhaar Resin 505 . .		150° C.	18–25	C.S. hydrocarbons		Water and alkali resistant finishes. For wood oil substitution.
KRUMBHAAR Resin 555 . .			110			Short rubbing and polishing varnishes.
Crestanol SB. 220		105°–114° C.	<20	C.S.H. drying oils and common solvents		For cheap media (not white) and varnishes. Yellows.
CRESTANOL SB. 221		98°–105° C.	<20	C.S. drying oils and common solvents I.S. methyl and ethyl alcohol	1·10	For cellulose lacquers and sanding sealers.
CRESTANOL SB. 222		110°–118° C.	<20	As SB. 221	1·09	As SB. 224 but yellows.
CRESTANOL SB. 224		110°–118° C.	<20	As SB. 221	1·09	For general purpose interior and exterior media (whites or colours) and varnishes.
CRESTANOL SB. 226		138°–148° C.	<20	As SB. 221	1·10	Quick drying durable varnishes. Overprint and rubbing varnishes.
CRESTANOL SB. 228		145°–155° C.	<20	As SB. 221	1·10	As SB. 226 but harder, quicker drying and more durable varnishes.

† EPOK R. 22A is similar to R. 22 but the tung oil has been eliminated.

CONSTANTS OF SYNTHETIC RESINS: PHENOLIC RESINS (MODIFIED)—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
CRESTANOL SB. 248		Viscous	18–24	C.S. drying oils and common solvents		Yellows. Quick drying, air-drying lacquers, stoving varnishes, nitrocellulose lacquers, spar varnishes, cement paint. Durable and chemical resistant varnishes,
CRESTANOL SB. 204	Modified cresol type	110°–120° C.	80–90	C.S. cyclic hydrocarbons C.S.H. drying oils		Stoving finishes.
CRESTANOL SB. 282	Modified cresol type	100°–105° C.	<20	C.S. aliphatic, aromatic and chlorinated hydrocarbons, esters, ketones C.S.H. drying oils		Stoving finishes.
Lewisol 1601	Lewisol 1501 combined with tung oil (3 : 1)	105°–125° C.	40	C.S. alcohols, esters, acetone P.S. aromatic hydrocarbons I.S. aliphatic hydrocarbons		Quick drying varnishes of good chemical resistance. Stoving lacquers.
LEWISOL 1602	Lewisol 1501 (100 lb.) combined with tung oil (94 lb.)	80°–90° C.	25	C.S. aromatic hydrocarbons, butyl alcohol I.S. aliphatic hydrocarbons		Durable, quick drying varnishes.
CR 102 †	Esterified	95° C. (F. Pt.)	15–20	C.S. hydrocarbons C.S.H. drying oils		Primers, undercoats, gold-sizes. Protective coatings for metals with wool grease.
CR 104–1	Rosin-oil modified, non-esterified	Plastic solid	55–65	C.S. alcohol, hydrocarbons C.S.H. drying oils		With dehydrated castor oil for Spec. 2× 17. Food can lacquers and chemical resistance.
CR 104–2	Oil modified	Plastic solid	90	As 104–1		Low stoving pasteurising lacquers.
CR 105–1	Rosin modified, non-esterified	98° C. (F.Pt.)	65–75	C.S.H. drying oils		Quick drying varnishes, gold-sizes, etc.

CR 105–2 . .	Rosin modified, low acid value	103° C. (F. pt.)	40	C.S. drying oils		Hard, quick drying vehicle for primers, etc. Chemical resistance. N.C. lacquers.
CR 106 . .	Rosin modified, esterified	105° C. (F.Pt.)	16–20	C.S.H. oils		Durable varnishes, primers, and gold-sizes.
CR 107 . .	High phenolic type, non-esterified	93° C. (F.Pt.)	60–70	C.H.S. oils		Quick drying primers and gold-sizes, marine and anti-fouling paints.
CR 112 . .	Rosin modified, high cresol	107° C. (F. pt.)	10–15	C.S.H. drying oils		Printing ink media. Durable varnishes.
CR 121 . .	Rosin modified, highly reactive, oil soluble	120° C. (F. pt.)	64	C.S. drying oils, aromatic hydrocarbons		Photogravure inks. Durable exterior varnishes. Quick drying primer and undercoat media.
CR 122 . .	As 121	118° C. (F. pt.)	15–20	As 121		As 121
Featalack CR 163	Rosin modified, cresol	105°–110° C.	70–80	C.S. aromatic hydrocarbons, drying oils		
FEATALACK CR 281	Rosin modified, cresol	105°–110° C.	115–120	C.S. alcohol, aromatic hydrocarbons, drying oils		
FEATALACK CR 301	Rosin modified, cresol	123°–129° C.	20–30	C.S. aromatic hydrocarbons, drying oils		
Beckacite 1100 . (R.C.I.)		121°–135° C.	15–20	C.S. acetates, coal-tar solvents C.S.H. turpentine and oils P.S. mineral spirits I.S. alcohols	1·10 1·14	Quick, hard drying varnishes, floor varnishes, media for porch and deck paints, four-hour enamels. Good water and chemical resistance.
BECKACITE 1101 . (R.C.I.)		*102°–111° C.*	*15–20*	C.S. acetates, coal-tar solvents, turpentine, drying oils P.S. mineral spirits I.S. alcohols	1·10 1·14	*Cheaper quick drying,* hard, durable varnishes.
BECKACITE 1102 . (R.C.I.)		102°–111° C.	15–20	C.S. acetates, coal-tar solvents, turpentine, drying oils P.S. mineral spirits I.S. alcohols	1·10 1·14	As 1101 but colour.

† Crayvallac resins.

CONSTANTS OF SYNTHETIC RESINS: PHENOLIC RESINS (MODIFIED)—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
BECKACITE 1106 (R.C.I.)		121°–135° C.	15–20	As 1100	1·10 1·14	As 1100 but colour.
BECKACITE 1108 (R.C.I.)		80°–90° C.	15–20	C.S. coal-tar solvents, turpentine C.S.H. drying oils P.S. mineral spirits I.S. alcohols, acetates	1·12 1·16	A cheap general purpose resin. Retards polymerisation of wood oil.
BECKACITE 1112 (R.C.I.)		110°–121° C.	15–20	C.S. acetates, coal-tar solvents, turpentine, drying oils P.S. mineral spirits I.S. alcohols	1·08 1·12	Quick drying pale non-yellowing lustrous varnishes and media. Water resistant. Durable.
BECKACITE 1113 (R.C.I.)		102°–111° C.	15–20	As 1112	1·10 1·14	As 1101 but colour.
BECKACITE 1116 (R.C.I.)		138°–154° C.	20–25	As 1100	1·10 1·14	A harder and faster drying resin than 1100.
Beckopol 1400 (R.C.I.)	Phenolated Congo copal	131°–150° C.	40–45	C.S. acetates, coal-tar solvents, turpentine C.S.H. drying oils P.S. mineral spirits I.S. alcohols	1·10 1·14	Hard rubbing and polishing varnishes. For quick setting and through drying.
Beckacite 100 P. (B.K.C.)	Reduced phenolic resin	119°–125° C. B. & R.	15–20			Hard gloss paints, low temperature coating and cold cut varnishes.
BECKACITE 1123 (B.K.C.)	As 100 P.	143°–149° C. B. & R.	15–20			Hard gloss paints. Industrial finishes. Quick drying varnishes with softer oils.
BECKACITE 1637 (B.K.C.)	As 100 P.	115°–123° C. B. & R.	130–145			Hard gloss paints and industrial finishes. Incompatible with basic pigments.
BECKACITE 1635 (B.K.C.)	As 100 P.	137°–143° C. B. & R.	120–135			As 1637 but soluble in methylated spirits and excellent for manila substitution.

BECKACITE 4892 (B.K.C.)	Pentaerythritol ester corresponding to 100 pale	148°–154° C. B. & R.	15–20		Yields quicker drying varnishes than 1123. Replaces Beckopol 1400 for rubbing varnishes.
BECKACITE 110G (B.K.C.)	Reduced cresylic resin	118°–124° C. B. & R.	15–20		As 120G but suitable for low temperature cooking, and for cold cut varnishes.
BECKACITE 120G (B.K.C.)	As 110G	144°–150° C. B. & R.	15–20		Low priced hard gloss paints and industrial finishes where colour not important. Printing inks, lino, etc.
BECKACITE 120GX (B.K.C.)	As 110G	144°–150° C. B. & R.	15–20		Identical with 120G but specially tested for solubility characteristics according to D.T.D. 375C.
BECKACITE 1621 (B.K.C.)	As 110G	138°–144° C. B. & R.	115–135		As 120G but incompatible with basic pigments.
BECKACITE 1623 (B.K.C.)	As 110G	120°–126° C. B. & R.	130–140		Similar to 1621 but softer. Insoluble in cold oil.
Erinite 11		83° C. (C. tube)	12	C.S. petroleum hydrocarbons, turpentine, xylol, etc. I.S. ethyl alcohol C.S. drying oils	Hard gloss media (including white pigmented media). Pale exterior and interior varnishes.
ERINITE 12		108°–115° C.	15	C.S. hydrocarbons and turpentine S.H. drying oils	Pale varnishes for interior and exterior. Printing inks. Gold stoving varnishes.
ERINITE 13	Phenolic resin modified with copal				
ERINITE 14		96° C. (C. tube)	9	C.S. linseed, perilla and tung oil P.S. turpentine, white spirit I.S. alcohol	Durable exterior varnishes. Flatting varnishes. Quick drying enamel media, and stoving enamel media.
ERINITE 16		120°–126° C.	25	C.S. hydrocarbons, turpentine S.H. drying oils	Stoving varnishes. Non-yellowing. Durable quick drying varnishes and enamels.

CONSTANTS OF SYNTHETIC RESINS: PHENOLIC RESINS (MODIFIED)—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
ERINITE 17		120°–126° C.	29	C.S. hydrocarbons, turpentine S.H. drying oils		Stoving varnishes. Non-yellowing. Durable quick drying varnishes and enamels.
ERINITE 18		111°–117° C.	15			Dark, hard durable quick drying varnishes. Printing inks.
ERINITE S. 210	Modified cresol type		High	C.S. alcohol, aromatic hydrocarbons		Similar to Albertol 61L.
Paradura C	High condensation content		30–35	C.S. aromatic hydrocarbons P.S. mineral spirits	1·10	Sanitary lacquers. Hard stoving enamels.
PARADURA 46	High condensation content		30–35	C.S. aromatic hydrocarbons P.S. mineral spirits	1·10	Durable spar varnishes. Media for industrial and house paints.
Glycophene NA				C.S. ethyl and butyl alcohols		Nitrocellulose lacquers.
GLYCOPHENE NB						For varnishes of low acidity. Metallic paint media.
GLYCOPHENE NC	Darker than NF, NL or NW			Soluble in oils at low temperatures		Cheap varnishes.
GLYCOPHENE NF				C.S. oils (warm)		Pale varnishes.
GLYCOPHENE NG				As NC but requires higher temperature treatment with oils		
GLYCOPHENE NL				As NF		As NF but yields harder films.
GLYCOPHENE NO	Polymerisable glycophene (oil modified phenolic)					Varnishes resistant to acids, alkalies and most organic solvents.
GLYCOPHENE NS		105°–115° C.		C.S. alcohols, esters, glycol ethers		Spirit varnishes, insulating varnishes. A shellac substitute.

GLYCOPHENE NV Solution	Combined glycophene (oil modified phenolic)					To improve oil varnishes by admixture.
GLYCOPHENE NX Solution	Combined glycophene (oil modified phenolic)					
GLYCOPHENE NW				Soluble in oils only after heat treatment		Quick, hard air-drying varnishes.
Resin 301†	Rosin modified phenol formaldehyde	80°–90° C.	15–20			Exterior varnishes and enamels.
Varcum 824	Rosin modified	115°–125° C.	80–90	C.S. mineral spirits and xylol I.S. alcohol, acetone	1·10	Aluminium media for wood primers. One coat interior enamel media. Cheap spar varnishes. Furniture rubbing varnishes, flat paint media, and baking primer surfacers.
R.H.C. Resin 5	Modified low cresol content	90°–95° C.	140–145	C.S. white spirit, drying oils		
R.H.C. 1301	Rosin modified. High cresol content	125°–127° C. (B. & R.)	140–150	C.S. aromatic hydrocarbons, butyl alcohol P.S. white spirit, alcohol and acetone C.S.H. drying oils		Shell and stoving varnishes.
R.H.C. 1302	Rosin modified. High cresol content	136°–140° C. (B. & R.)	135–145	As for 1301 but higher temperatures required for oils		Hard resin suitable for shell varnishes, anti-gas paints and stoving varnishes.
R.H.C. 1303	Rosin modified. High cresol content. Contains zinc	144°–148° C. (B. & R.)	25–30	C.S. aromatic hydrocarbons I.S. alcohols, white spirit		Paint media.
R.H.C. 1100	Esterified modified cresol resin	95°–126° C. (B. & R.)	12–15	C.S. aromatic hydrocarbons, esters and white spirit C.S.H. drying oils I.S. alcohols		Copper wire enamels, chemical resistant finishes, boat varnishes, abrasion retant finishes.
R.H.C. 1200	Esterified modified cresol resin	115°–126° C. (B. & R.)	15–20	As 1100		As 1100.
R.H.C. 1201	Esterified modified cresol resin	125°–136° C. (B. & R.)	20–25	As 1100 but some stronger solvents necessary with white spirit		As 1100.

† *Uhlhorn Bros.*

CONSTANTS OF SYNTHETIC RESINS: PHENOLIC RESINS (MODIFIED)—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
R.H.C. 1202	Esterified modified cresol resin	132°–144° C. (B. & R.)	20–25	As 1201		As 1100.
R.H.C. 1800	Esterified modified cresol resin	105°–120° C. (B. & R.)	15–20	As 1100		As 1100.
Amberol B/S–1		121°–129° C. B. & R.	12–18	C.S. aromatic hydrocarbons, turpentine, hydrogenated naphthas P.S. white spirit I.S. alcohol C.S.H. drying oils	1·09	Quick drying interior varnishes and enamels.
Amberol F 7		142°–149° C. B. & R.	12–18	As above	1·10	A versatile resin for short oil rubbing varnishes. Printing inks.
Amberol F 77		145°–154° C. B. & R.	< 20	As above	1·11	Similar to F7 but specially suitable for soft oil varnishes. Better drying, higher viscosity, and better alkali and water resistance than F 7.
Amberol K 12A		150°–160° C. B. & R.	100–132	C.S. aromatic hydrocarbons P.S. white spirit, turpentine hydrogenated naphthas I.S. alcohol C.S.H. oils	1·10	Rubbing varnishes, quick drying primers, hard, quick drying baking enamels.
Amberol M 82		127°–133° C. B. & R.	12–18	C.S. white spirit, hydrogenated naphthas, turpentine, aromatic hydrocarbons I.S. acetone, alcohol C.S.H. drying oils	1·10	Pale varnishes, with good alkali resistance. High white spirit tolerance.
Amberol M 86		150°–158° C. B. & R.	12–18		1·08	
Amberol M 88		161°–169° C. B. & R.	12–18		1·07	
Amberol M 93		172°–180° C. B. & R.	12–18	As M 82, 86 and 88 but P.S. in white spirit	1·08	Substitute oil formulations.

AMBEROL 226 .		66°–72° C. B.& R.	75–85	C.S. acetone, alcohol P.S. turpentine, aromatic hydrocarbons I.S. white spirit C.S.H. drying oils	1·15	Durable long tung oil varnishes. Quick drying and good adhesion.
Durez 210 . .	Isomerised terpene-phenol resin. Free from rosin or ester gum	115°–120° C.	15–20	C.S. mineral spirits, coal-tar solvents, hydrogenated naphthas, aliphatic esters P.S. butyl alcohol I.S. ethyl alcohol Compatible with drying oils	1·086	Gives quicker set than Durez 500, 525, or 550. Non-yellowing. General purpose non-skinning varnishes, deck, floor, etc., and in printing ink media. Not so durable as 500, 525, 570.
DUREZ 330 .	Highly polymerised. Thermoplastic	Liquid	30	C.S. aromatic hydrocarbons and oils I.S. alcohol P.S. aliphatic hydrocarbons	1·065	
DUREZ 11933 .	As 330	Liquid	40	As 330	1·088	
DUREZ 209 .	Isomerised terpene, phenolic. Thermoplastic	100°–110° C. (capillary)	95–105	C.S. hydrocarbons, alcohols, esters, ketones C.S.H. drying oils	1·094	
DUREZ 219 .	As 209	138°–141° C. (capillary)	50–60	C.S. hydrocarbons I.S. alcohol C.S.H. drying oils	1·085	
DUREZ 220 .	As 209	138°–141° C. (capillary)	17–22	As 219	1·080	
DUREZ 230 . .	As 209 but high viscosity type	135°–142° C. (capillary)	15–20	C.S. aromatic hydrocarbons I.S. aliphatic hydrocarbons, alcohol C.S.H. drying oils	1·115	
DUREZ 11036 .	As 230	38°–145° C. (capillary)	25–35	As 230	1·116	
DUREZ 50660 .	Isomerised terpene phenolic. Thermoplastic Special type	94°–96° C. (capillary)	0	C.S. hydrocarbons I.S. alcohol C.S.H. drying oils	1·082	

CONSTANTS OF SYNTHETIC RESINS: PHENOLIC RESINS (MODIFIED)—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
DUREZ 50821 .	As 50660	135°–141° C. (capillary)	10–15	C.S. aromatic hydrocarbons I.S. alcohols P.S. aliphatic hydrocarbons C.S.H. drying oils	1·085	
DUREZ 334 .	As 50660	Liquid	30–34	C.S. hydrocarbons, esters, ketones, drying oils I.S. alcohol		
DUREZ 50800 .	As 50660	Liquid	55–65	As 334	1·029	

CONSTANTS OF SYNTHETIC RESINS: POLYSTYRENE RESINS

Distrine 3 .	Polystyrene	70°–75° C.		C.S. aromatic hydrocarbons		
DISTRINE 30 .	Polystyrene	110°–120° C.		As 3		
DISTRINE 80 .	Polystyrene	160°–180° C.		As 3		
P.M.S. RESIN .	Poly-*p*-methyl styrene	80°–85° C.		As 3		

CONSTANTS OF SYNTHETIC RESINS: SILICONE RESINS

Dow Corning 993 (50 % solids) .	Silicone	Liquid			1·005	Heat resistant, waterproof varnishes for impregnating.
DOW CORNING 996 (60 % solids .	Silicone	Liquid			1·050	As above but low baking type.
DOW CORNING 2102 (60 % solids in toluol) . .	Silicone	Liquid				Thermosetting resin. Bonding resin for electrical insulation, and for glass and lens cements.
DOW CORNING 2103 (60 % solids in toluol) . .	Silicone	Liquid				Thermosetting resin. Bonding agent for glass and asbestos cloth.

DOW CORNING 801 (70 % solids in Solvesso No. 2)	Silicone	Liquid				Coatings resistant to heat, moisture, oxidation and ultra-violet rays.
DOW CORNING 803 (50 % solids in toluol) . . .	Silicone	Liquid				

CONSTANTS OF SYNTHETIC RESINS: SYNTHETIC SPIRIT SOLUBLE RESINS (MISCELLANEOUS)

Albertol K. 6S .	Spirit soluble copal type	105° C. (S. pt.) 115° C. (F. pt.) 150° C. (Fl. pt.)	<20	C.S. acetone, esters, alcohols I.S. aromatic hydrocarbons, chlorinated hydrocarbons, turps, mineral spirits and drying oils	1·219	Spirit varnishes and cellulose lacquers. Hard resin with good electrical resistance, dries free from residual tack, slight yellowing tendency.
ALBERTOL 35K .	Spirit soluble copal type	85° C. (S. pt.) 95° C. (F. pt.) 130° C. (Fl. pt.)	<20	As K. 6S but, P.S. aromatic hydrocarbons	1·181	Darker and softer than K. 6S, otherwise similar. Varnishes with good electrical resistance.
ALBERTOL 110K .	Spirit soluble copal type	90° C. (S. pt.) 100° C. (F. pt.) 140° C. (Fl. pt.)	<20	97% sol. in methylated spirits, otherwise as 35K	1·220	Darker than 35K but harder. For black or dark spirit varnishes. Varnishes with good electrical resistance.
ALBERTOL 844K .	100% cresol formaldehyde			C.S. ketones, alcohols, esters I.S. hydrocarbons		Spirit soluble. Acid resistant finishes. Good electrical resistance.
ALBERTOL SHELLAC . .		95° C. (S. pt.) 105° C. (F. pt.) 140° C. (Fl. pt.)	<20	C.S. acetone, esters, alcohols P.S. aromatic hydrocarbons I.S. mineral spirits, drying oils	1·180	French polishes and matt finishes. Yellows slightly and is less elastic than natural shellac.
Erinite 1 . .		79°–85° C.	160	C.S. alcohol		A spirit Manila substitute for white line paint media.
ERINITE 1A .		92°–96° C.	181			

CONSTANTS OF SYNTHETIC RESINS: SYNTHETIC SPIRIT SOLUBLE RESINS (MISCELLANEOUS)—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
ERINITE 2		85°–91° C.	175	C.S. alcohol		A spirit Manila substitute for white line paint media. Spirit inks. Spirit varnishes.
ERINITE 2A		98°–104° C.	196			
ERINITE 100	Pure cresylic acid resin	50°–56° C.	49	C.S. alcohol	1·202	For coloured lamp lacquers.
Teglac 128		145°–155° C.	265–285	C.S. alcohol		Lacquers, varnishes and inks.
Bedesol 1130	Thermo-hardening resin	66°–95° C.		C.S. ketones, alcohols, esters I.S. hydrocarbons	1·198	To improve water resistance of PARALAC 2001. Paper adhesives and insulating lacquers.
Durophene 70U	Contains phenol. Thermosetting	Liquid		C.S. methylated spirits		Strong phenolic odour. Varnishes with high electrical resistance. As binding and impregnating media for electrical purposes.
DUROPHENE 71V	Phenol free. Thermosetting	Liquid		C.S. methylated spirit		Faint pleasant odour. Pale colour and fast to light. For transparent or pigmented stoving lacquers.
DUROPHENE 72W/33.	Phenol free. Thermosetting	Solid		C.S. methylated spirit		Free from phenolic odour. Use where odour of 77B is objectionable.
DUROPHENE 75Z/33.	Phenol free. Thermosetting	Solid		C.S. methylated spirit		
DUROPHENE 76A	Phenol free. Thermosetting	Liquid		C.S. methylated spirit		Faint odour only. Uses as 70U.
DUROPHENE 77B	Contains phenol. Thermosetting	Solid		C.S. methylated spirit		Phenolic odour. Electrical lacquers. Heat and oil resisting, insoluble films after stoving. Resistant to acids, soda and ammonia.

Durez 175 .	Thermosetting. Pure phenolic	65°–75° C. (capillary)	20–25	C.S. alcohol, esters, ketone I.S. hydrocarbons and drying oils	1·250	
Durez 333 .	Thermosetting. Pure phenolic	Liquid	35	As 175	1·300	
Durez 50344 .	Thermosetting. Pure phenolic	Liquid	75	As 175	1·222	
Durez 50801 .	Thermosetting. Pure phenolic	Liquid	15	As 175	1·034	
Durez 50817 .	Thermosetting. Pure phenolic	Liquid	20	As 175	1·006	
Durez 50824 .	Thermosetting. Pure phenolic	Liquid	65	As 175	1·207	
Phenol Resin R. 63 † . .		98°–110° C.	149	C.S. alcohol		
Phenol Resin R. 65 † . .		79°–91° C.	157	C.S. alcohol		
Phenol Resin R. 66 † . .		70°–83° C.	165	C.S. alcohol		
Wresin 58 . .	Modified cresol formaldehyde	105° C.	140	C.S. white spirit, methanol		Road line paints
Wresin 60 .	Modified cresol formaldehyde			C.S. alcohols		Dark corrosion resistant, high temperature stoving lacquers. Stoving finishes.
Wresin 61 .	Modified cresol formaldehyde		27	C.S. alcohols		Plasticiser for 60.
Wresin PF 129 .	Pure cresol formaldehyde		44	C.S. alcohols, ketones (esters)		Can lacquers.
Wresin PF 70 .	Pure cresol formaldehyde	73° C.	26	C.S. alcohols, ketones (esters)		Electrical insulation and stoving finishes.
Wresin 51 .	Pure phenol formaldehyde	90°–92° C.	60	C.S. alcohols, ketones (esters)		Petrol and hydrocarbon resistant coatings. Spirit lacquers.
Wresin 54 .	Pure cresol formaldehyde	85°–87° C.	60	As 51		As 51.
Wresin 55 .	Pure cresol formaldehyde 67% solids in meth.			C.S. alcohols		Food can lacquers. Hardener for Wresin 60.
Epok R. 500 .	Cresol formaldehyde. Thermosetting	43°–48° C.				

† J. Beadel & Co., Ltd.

CONSTANTS OF SYNTHETIC RESINS: SYNTHETIC SPIRIT SOLUBLE RESINS (MISCELLANEOUS)—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
Epok R. 503	Cresol formaldehyde. Thermosetting	50°–55° C.				
EPOK R. 506	Cresol formaldehyde. Thermosetting	50°–55° C.				
EPOK R. 600	Cresol formaldehyde. Thermosetting	60°–65° C.				
EPOK J 843/60	Cold setting phenolic lacquer. 60% solids in 90 parts 74 OP. meth. and 10 parts ethyl acetate. Castor oil base plasticiser present	Liquid	3·5 *p*H	C.S. alcohols, esters and ketones	1·09	When acid catalysts are added for airscrew, marine and non-slip floor finishes. Quick build wood finishes, and heat resisting table top lacquers.
Beckacite 1635 (B.K.C.)	Reduced phenolic resin	135°–143° C. B. & R.	120–135	C.S. alcohol		Clear varnishes and enamel media with non-reactive pigments. Substitute for shellac and Manila copal in spirit varnishes.
BECKACITE 1624 (B.K.C.)	Reduced cresylic resin	97°–103° C. B. & R.	135–145	C.S. alcohol, methanol		Low priced spirit soluble resin for manila replacement, where colour unimportant.
Bakelite V 11098	Thermosetting. Phenol-formaldehyde resin in butyl alcohol 74% solids	Liquid		C.S. butyl alcohol or mixtures with high flash solvent naphtha; esters, ketones	1·025	Stoving food can lacquers.
BAKELITE R 804	Heat reactive			C.S. acetone, esters, alcohols		Stoving varnishes for surface coating and electrical insulation.
BAKELITE R 4697	Heat reactive			As R 804		As R 804.
BAKELITE R 5363	Heat reactive			As R 804		As R 804.
BAKELITE R 5468	Non-heat reactive	82°–86° C.		C.S. acetone, esters, alcohols		Air-drying petrol resistant paints.
R.H.C. 2	Modified, low cresol content	95°–105° C.	160–170	C.S. alcohol P.S. methanol C.S.H. drying oils		Spirit Manila substitute. Road-line paints.

R.H.C. 3 . .	Modified, low cresol content	90°–95° C.	140–145	C.S. alcohol P.S. methanol		Spirit Manila substitute. Gold stoving varnishes.
R.H.C. 4 . .	Modified, low cresol content	115°–125° C.	120–140	C.S. alcohol P.S. methanol		Spirit Manila substitute. Shell varnishes. Paint media with non-reactive pigments.
CR 103 . .	Rosin modified. Non-esterified	75° C. (F. pt.)	120	C.S. alcohol		Road-line paints and insulating varnishes.
CR 108 . .	Pure cresol unmodified. Non-thermosetting	70° C. (F. pt.)	8–15	C.S. alcohol		Petrol and oil resisting finishes. Insulating varnishes.
CR 113 . .	Liquid thermosetting cresol-formaldehyde resin		Slightly alkaline	C.S. alcohols		High temperature stoving enamels. Food can lacquers.
CR 116 . .	Cold setting cresol formaldehyde			C.S. alcohols		Cold setting glues and cements. Brush and electric bulb cements.
CR 117 . .	Liquid thermosetting		As above	C.S. alcohols		As 113 but low tempearture stoving.
CR 124 . .	Liquid thermosetting, modified		As above	C.S. alcohols		Flexible finishes. Bonding and laminating cements. Food can lacquers.
CR 125 . .	Liquid thermosetting, modified		As above	C.S. alcohols		As 124 but not quite so flexible.
CR 126 . .	Pure xylenol formaldehyde. Non-thermosetting	70° C. (F. pt.)	8–15	C.S. alcohols		Petrol and oil resisting paints. Insulating varnishes. Food can lacquers.

CONSTANTS OF SYNTHETIC RESINS: UREA RESINS

UREA SOLUTION 2562A (Paramet Chemical Corporation)	60% solids 40% butanol		0·5–1·0	C.S. aromatic hydrocarbons P.S. mineral spirits	1·03	For refrigerator finishes and pale non-yellowing lacquers.
Beckamine 3440 (R.C.I.)	60% solids 40% *n*-butanol		5–7	C.S. aromatic hydrocarbons, alcohols, esters	1·030	For non-yellowing stoving finishes. For hardening stoving alkyd finishes.
BECKAMINE P. 138 (R.C.I.)	Etherified urea formaldehyde 60% solids 20% toluol 20% butanol		4–6		1·025	Baking enamels with alkyds. Good colour retention and light fastness.

CONSTANTS OF SYNTHETIC RESINS: UREA RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
BECKAMINE P138 (B.K.C.)	Butanol etherified U.F. 60 % solids in xylol—butanol		2·5–3·5	Fair white spirit tolerance	1·035	Industrial stoving whites for refrigerators, etc. Excellent for infra-red stoving. Non-yellowing, mar-proof rapid stoving finishes.
BECKAMINE P201 (B.K.C.)	Butanol etherified U.F. 80 % solids in butanol		3–5			
BECKAMINE P426 (B.K.C.)	Unmodified U.F. 50 % solution in water		$p_H = 7$	C.S. water	1·235	For improving wet strength retention of paper.
Beetle RESIN (1) (B.E. 621) C.A. Solution	46% solids 54% butanol		5	C.S. mixture of aromatic hydrocarbon and alcohol	0·90	Hardens faster than UF or UG resins. Not so compatible with alkyds.
BEETLE RESIN UF (B.E. 605)	60% solids 40% butanol		7	C.S. aromatic hydrocarbons, alcohols		
BEETLE RESIN UG (B.E. 610)	60% solids 40% butanol		2–3	As above	1·05	Hard stoving finishes. Good adhesion. Light and heat resistant.
BEETLE RESIN HT Mod. urea	43% solids 57% thinners		15–20	C.S. 6/xylol 2/butanol 1/ethyl lactate	1·05	Glossy, heat resisting finishes.
BEETLE RESIN CR 2. Mod. urea (B.E. 620)	50% solids 50% thinners			C.S. xylol, Cellosolve and acetone mixture		Crackle stoving finishes.
BEETLE RESIN 58 B.E. 611	60% solids 40% thinners		5–6	C.S. coal-tar or petroleum hydrocarbons. Turpentine	1·05	Slow setting enamels for roller coating and brushing.
BEETLE 212–9	60% resin 6% octyl alcohol 24% butanol 10% Solvesso 3		1–2	C.S. white spirit		Slow initial set and good flow. Roller coating and stoving enamels.
BEETLE 219–8	50% resin 30% butanol 20% xylol		4–6	P.S. white spirit		Stoves in range 225°–250°.

BEETLE 227–8 .	50% resin 30% butanol 20% xylol		3–5	As 219–8		General purpose unmodified urea resin.
BEETLE 592–8 .	Alkyd modified urea 50% resin 25% butanol 25% xylol		3–8	As 219–8		Stoving enamels.
BEETLE RESIN 3000 B.E. 617	(Mod. urea) 50% solids 50% thinners		7–8	Mixture of aromatic hydrocarbons and alcohols	1·00	Flexible white enamels. Cellulose lacquers.
Paralac 2001 .	Thermohardening, free from drying oil, with 54 % Cellosolve		27·5–35·0 (solid resin)	C.S. ketones, higher alcohols. Mixtures of alcohols and aromatic hydrocarbons	1·085–1·093	Rapid hardening stoving finishes. Non-yellowing on stoving.
PARALAC 2101 .	As 2001 type but 58 % Cellosolve		33–40 (solid resin)	As 2001		As 2001.
PARALAC 3101 .	Thermohardening, free from drying oil, with 51 % solvent. (Solvent is mixture of ethyl lactate and butyl alcohol)		65–90 (solid resin)	C.S. Cellosolve, ethyl lactate, sextol, sextone, pine oil P.S. aromatic hydrocarbons	1·068–1·678	Clear stoving lacquers. Resistant to discoloration up to 180° C.
PARALAC 4001 .	50% soln. in xylene butanol			C.S. aromatic hydrocarbons, alcohols	1·020	Hard, pale, stoving finishes. Light and heat resistant.
PARALAC 5001 .	50% soln. in xylene butanol			As 4001	1·020	As 4001.
Uformite F–200E	Urea 50 % solids 25 % xylol 25 % butanol		0·5–2·0	C.S. alcohols, esters, ketones, cellosolve, cellosolve acetate	1·02	Stoving finishes which are colourless and non-yellowing, with good solvent and chemical resistance.
UFORMITE F–226E	Urea 50 % solids 50 % capryl alcohol		2·0–3·5	As above	0·98	As above.
UFORMITE F–301.	Alkyd modified urea 60 % solids 10 % xylol 30 % butanol		1–4	As above	1·04	As above.

CONSTANTS OF SYNTHETIC RESINS: VINYL RESINS

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
Alvar 2·5/70	Polyvinyl acetal	120° C. Kraemer and Sarnow	0·0	C.S. alcohol, esters, aromatic hydrocarbons, ketones I.S. aliphatic hydrocarbons, drying oils, turpentine, etc.	1·14	Hard, tough lacquers. Thermoplastic moulding powders.
ALVAR 480	As 2·5/70	146° C. Kraemer and Sarnow	0·0	As 2·5/70	1·14	As 2·5/70.
ALVAR 770	As 2·5/70	160° C. Kraemer and Sarnow	0·0	As 2·5/70	1·14	As 2·5/70.
ALVAR 1570	As 2·5/70	170° C. Kraemer and Sarnow	0·0	As 2·5/70	1·14	As 2·5/70.
ALVAR 1580	As 2·5/70	180° C. Kraemer and Sarnow	0·0	As 2·5/70	1·14	As 2·5/70.
Vinylite AYAA	Polymerised vinyl acetate			C.S. methanol and lower boiling alcohols containing a small percentage of water, ketones esters, ether alcohols, chlorinated hydrocarbons, lower aromatic hydrocarbons I.S. petroleum hydrocarbons, glycols, turps, vegetable and mineral oils	1·191 (20° C.)	
VINYLITE AYAF	Polymerised vinyl acetate				1·191 (20° C.)	
VINYLITE AYAT	Polymerised vinyl acetate				1·191 (20° C.)	
VINYLITE AYAV	Polymerised vinyl acetate					
VINYLITE AYAW	Polymerised vinyl acetate					
VINYLITE QYNA	Polymer of vinyl chloride			C.S. methyl *n*-amyl ketone, methyl isobutyl ketone, cyclohexanone, isophorone and acetyl acetone	1·406	

VINYLITE V series	Copolymers of vinyl acetate and vinyl chloride		0·0	*Low molecular weight co-polymers* C.S. ketones, esters, chlorinated hydrocarbons, dioxan, propylene oxide *Higher molecular weight co-polymers* C.S. dioxan, ethylene dichloride, acetonyl acetone, mesityl oxide, and higher ketones including methyl iso-butyl ketone, cyclohexanone, isophorone	1·34–1·36	Alkali and acid resisting lacquers, metal lacquers, impregnating varnishes for paper, felt, etc., insulating lacquers.
VINYLITE X series	Polyvinyl butyral			C.S. alcohols, glycol ethers, dioxan, esters I.S. aliphatic hydrocarbons P.S. ketones, aromatic and chlorinated hydrocarbons	1·11	Light and heat resistant lacquers. Less chemical resistance than V or Q series.
Resovyl NFF	Acetate. Very highly condensed			C.S. hydrocarbons, alcohols, most organic solvents		In colourless, odourless, tasteless lacquers of good light resistance. Straw hat lacquers. Translucent paper sizes. NC is compatible with nitrocellulose.
RESOVYL NC	Acetate					
RESOVYL NM	Acetate. Less viscous type					
RESOVYL ND	Moderately condensed					
Mowilith HX (10% soln. in ethyl acetate)	Polyvinyl acetate			C.S. chlorinated hydrocarbons, acetone, esters, aromatic hydrocarbons (benzol and toluol); glycols, some alcohols I.S. pure xylol, isopropyl alcohol, butyl alcohol, aliphatic hydrocarbons, turps, ether	1·173 (20° C.)	Impregnating media for textiles, artificial leather, roofing compositions, metal lacquers, primers for wood, nitrocellulose lacquers, heat resisting lacquers, anti-shatter lacquers, cements, adhesives.
MOWILITH 115	Polyvinyl acetate				1·163	
MOWILITH H	Polyvinyl acetate	Softening point 105°–125° C.			1·170	
MOWILITH N	Polyvinyl acetate	Softening point 90°–110° C.			1·171	
MOWILITH NN	Polyvinyl acetate	Softening point 60°–80° C.			1·205	

CONSTANTS OF SYNTHETIC RESINS: VINYL RESINS—*Continued*

Reference.	Remarks.	M.Pt.*	Acid Value.	Solubility.	S.G.	Recommended Uses.
Crestavin R		Softening point 180° C.		C.S. acetone benzol, toluol, alcohols, chlorinated hydrocarbons, esters I.S. higher alcohols, dipentene, vegetable oils, ether, glycols, aliphatic alcohols, turps, xylol	1·19	Adhesives, anti-shatter lacquers, luminous paint media, impregnating varnish for paper, wood and metal primers, printing inks.
CRESTAVIN P		Softening point 170° C.			1·19	
CRESTAVIN N		Softening point 140° C.			1·19	
CRESTAVIN D		Softening point 120° C.			1·19	
CRESTAVIN S		Softening point 95° C.			1·19	
CRESTAVIN C		Softening point 70° C.			1·19	
CRESTAVIN J		Softening point 55° C.			1·19	

CONSTANTS OF SYNTHETIC RESINS: ZINC RESINATES

Ziro RESIN	Zinc hardened rosin (4·8% Zn)	121° C.	15			Nitrocellulose furniture lacquers.
ZIREX RESIN	Zinc resinate type (8·75 % Zn)	130°–135° C. (capillary)	0·0	C.S. mineral spirits	1·16	Non-feeding media with tung oil. Good wetting and hardening properties. Floor enamel media. Better durability than ester gum.
ZITRO RESIN	Less zinc than Zirex resin (4·8% Zn)	130°–135° C. (capillary)	15·0	C.S. mineral spirits	1·13	
Erinite 430	Zinc resinate (4·5% Zn)	100°–106° C. (B. & R.)	15–20	C.S. white spirit, drying oils P.S. xylol I.S. alcohol and methanol		Road-line paints, quick drying paints, N.C. lacquers.
Frebol G.P.S.C.	Zinc resinate. 9·6% Zn, 1.9% Ca	139° C.	(6–7%)			
FREBOL G.P. (plasticised)	Zinc resinate soln. in white spirit 9·6% Zn 54% solids					

ZINAR . .	5·6% Zn	158°–162° C. (capillary)	0	C.S. hydrocarbons, terpenes, esters, ethers, drying oils I.S. alcohols	1·15	
ZIKOL . .	65% zinc resinate (7·2% Zn), soln.	Liquid	6–10		0·996	
ZINOL . .	64% zinc resinate (7·2% Zn) soln.	Liquid	6–10		0·982	
Wresinate "Z".	54% solution in white spirit. Zn content 9·6%					For through drying, hardening and pigment dispersion. To promote wetting and to eliminate skinning and wrinkling.
WRESINATE solid	Solid zinc resinate (10·8% Zn)	170° C.		C.S. hydrocarbons, terpenes, etc.		As Wresinate Z.
WRESINATE 92 .	54% zinc resinate in xylol (10·6% Zn)					As Wresinate Z.
Beckacite 314 . (B.K.C.)	60% zinc resinate in white spirit (5·7% ash)			C.S. hydrocarbons, drying oils, etc.		Media for paints and enamels. Compatible with basic pigments. Good wetting properties. Cheap floor varnishes.
Epok R55 .	Oil modified zinc resinate	135°–140° C.	25–30	C.S. drying oils and aliphatic hydrocarbons		Quick drying gold sizes.
EPOK R654 .	Oil modified zinc resinate	120°–130° C.	20–25	As R55		Gloss paint media.
EPOK R984 .	Zinc resinate (12% Zn)	90°–100° C.	20–25	As R55		Adhesives, gloss paints, plaster primers.
EPOK R647/65 .	Zinc resinate soln. (15% ZnO)		20–25	As R55		Very pale resin. Paper varnishes, road line paints, etc.

SYNTHETIC RESINS—THEIR TRADE NAMES AND SUPPLIERS

Trade Name	Supplier
Acryloid	Resinous Products and Chemical Co.
Albertol	I.C.I. Ltd.
Alprokyd	I.C.I. Ltd.
Alvar	Shawinigan Products Corp.
Ambeslac	Resinous Products and Chemical Co.
Amberol	Resinous Products and Chemical Co.
Arochem	Stroock and Wittenberg Corp.
Arochlor	Monsanto Chemical Co.
Arofene	Stroock and Wittenberg Corp.
Aroplaz	Stroock and Wittenberg Corp.
A.W. 2	J. M. Steele.
Bakelite	Bakelite Ltd.
Beckacite	Reichold Chemicals Inc.*
Beckamine	Reichold Chemicals Inc.*
Beckolin	Beck Koller & Co. Ltd.*
Beckopol	J. Beadel & Co. Ltd.
Beckosol	J. Beadel & Co. Ltd.
Bedacryl	I.C.I. Ltd.
Bedesol	I.C.I. Ltd.
Beetle	Barter Trading Corp. American Cyanamide and Chemical Corp.
Clophen A.	J. M. Steele.
Crayvallac (C.R.)	Cray Valley Products.
Crestanol	Scott Bader & Co. Ltd.
Crestavin	Scott Bader & Co. Ltd.
Crestin	Scott Bader & Co. Ltd.
Distrine	British Res Ltd.
Dow Corning (D.C.)	Dow Corning Corp.
Duraplex	Resinious Products and Chemical Co.
Durecol	Établssements Kuhlmann.
Durez	Durez Plastics and Chemicals Inc.
Epok	British Resin Products Ltd.
Erinite	A. Boake Roberts Co. Ltd. Erinoid Ltd.
Falkyd	Falk & Co.
Falkote	Falk & Co.
Featalack	Featly Products Ltd.
Frebol	Fredk Boehm Ltd.
Glycophene	Établissements Kuhlmann.
Glycolac	Établissements Kuhlmann.
Glycopal	Établissements Kuhlmann.
Glycodione	Établissements Kuhlmann.
Glyptolac	Cray Valley Products Ltd.
Hercolyn	Hercules Powder Co.
K.M.	J. M. Steele & Co.
Krumbhaar	Krumbhaar Corp.
Lewisol	Hercules Powder Co.
Melmac	American Cyanamid and Chemical Corp.
Mowilith	Advance Solvents and Chemical Co.
Nevillac	The Neville Co.
Neville	The Neville Co.
Nevillite	The Neville Co.
Nevindene	The Neville Co.
Nuba	The Neville Co.
Paradene	The Neville Co.

Paradura	Paramet Chemical Corp.
Paralac	I.C.I. Ltd.
Paranol	Paramot Chemical Corp.
Parapen	Paramot Chemical Corp.
Paraplex	Resinous Products and Chemical Co.
Petrex	Hercules Powder Co.
Phenac	American Cyanamid and Chemical Corp.
Phenester	The Neville Co.
Resovyl	Établissements Kuhlmann.
Rezyl	American Cyanamid and Chemical Corp.
R.H.C.	R. H. Cole & Co. Ltd.
R.I.	Rubber Industries Ltd.
Synolac	Cray Valley Products Ltd.
Teglac	American Cyanamid and Chemical Corp.
Texyn	Scott Bader & Co. Ltd.
Uformite	Resinous Products and Chemical Co.
Varcum	Varcum Chemical Corp.
Velsicol	Velsicol Corp.
Vinylite	Carbide and Chemicals Corp.
Wresin	British Paints Ltd.
Zikol	Newport Industries Inc.
Zinar	Newport Industries Inc.
Zinol	Newport Industries Inc.
Zirex	Newport Industries Inc.
Zitro	Newport Industries Inc.

* In the foregoing tables those products marked R.C.I. (Reichhold Chemicals Inc.) are of American origin ; those marked B.K.C. (Beck Koller & Co. (England) Ltd.) are British.

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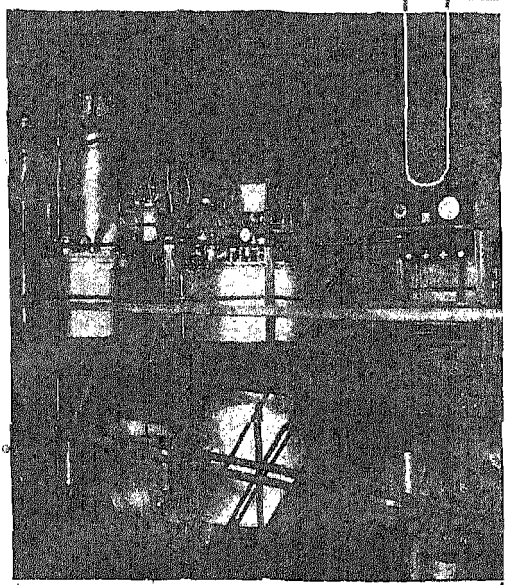

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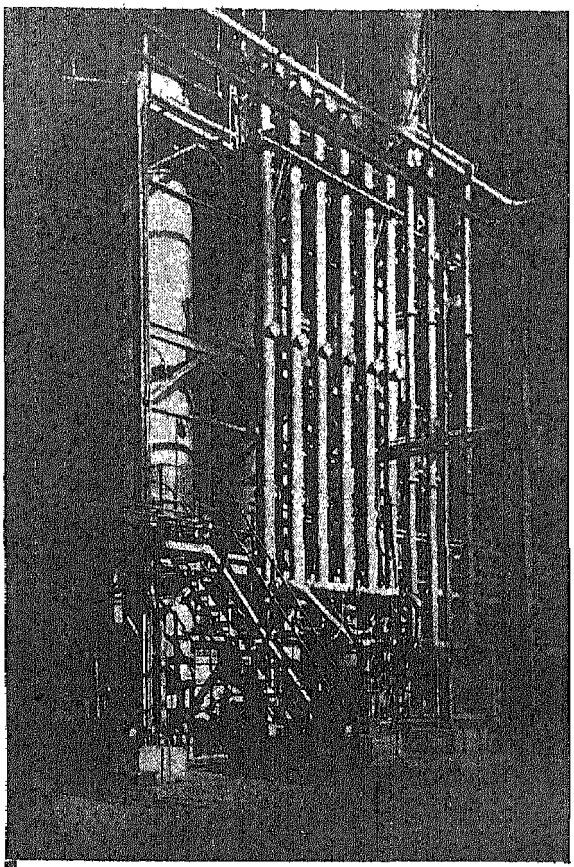

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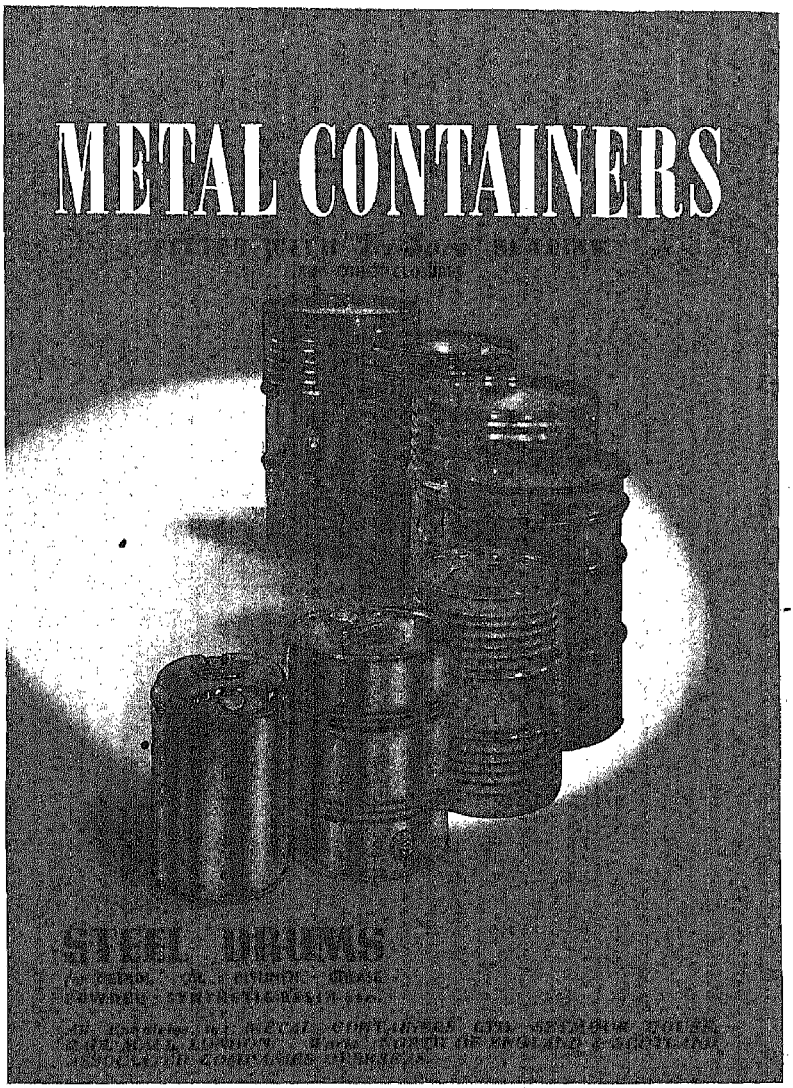

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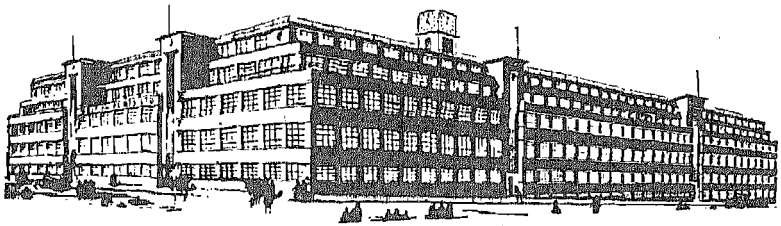

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